STUDY OF INTRINSIC VISCOSITY AND FLOW ACTIVATION ENERGY OF SOME POLYMERS IN DIFFERENT SOLVENTS

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by

RABAB IMAD A. AL-JBOORI
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I certify that this thesis entitled **"Study of Intrinsic Viscosity and Flow Activation Energy of Some Polymers in Different Solvents"** was prepared by **Rabab Imad Ahmed Al-Jboori** under my supervision at Nahrain University / College of Engineering in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

Signature: T. Kashmoul
Name: Prof. Dr. Talib B. Kashmoula
(Supervisor)
Date: 12/05/2011

Signature:
Name: Asst. Prof. Dr. Basim O. Hasan
(Head of Department)
Date: 26/5/2011

Certificate

We certify, as an examining committee, that we have read this thesis entitled "**Study of Intrinsic Viscosity and Flow Activation Energy of Some Polymers in Different Solvents**", examined the student (**Rabab Imad Ahmed Al-Jboori**) in its content and found it meets the standard of thesis for the degree of Master of Science in Chemical Engineering.

Signature T. Kashmoula
Name: Prof. Dr. Talib B. Kashmoula
(Supervisor)
Date: 15 /05/ 2011

Signature: Wadood
Name: Asst. Prof. Dr. Wadood Taher
(Member)
Date: 17 / 5 /2011

Signature: K.S. Abdulmasih
Name: Dr. Kamal S. Abdulmasih
(Member)
Date: 17 /5 /2011

Signature: S/Al Naimi
Name: Prof. Dr. Safa A. Al-Naimi
(Chairman)
Date: 19 / 5 / 2011

Approval of the College of Engineering

Signature: M. J. Jweeg
Name: Prof. Dr. Muhsin J. Jweeg
(Dean)
Date: 26 / 5 /2011

Abstract

The intrinsic viscosity and flow activation energy have been studied for several polymers which is used in some industrial applications, such as polyisobutylene of types Oppanol B150, 200, and 250 with different molecular weights of 2.5, 4.1 and 5.9 million g/mole, respectively, which dissolve in crude and gas oil. In addition three types of additives brought from Al-Dura refinery; olefin copolymer (OCP), {viscoples-4-677, viscoplex-215496, and Lubrizol R 7077} which dissolved in crude oil, and the polymers which is soluble in water such as polyacrylamide with high molecular weight and xanthan gum with molecular weight 3.7 million g/mole were also studied.

Measurements of intrinsic viscosity and Huggins constant have been carried for all types of polymers listed above, at a temperature of 40 and 100°C using a capillary viscometer.

It was found that the intrinsic viscosity of polyisobutylene decreases as the temperature of crude and gas oil increase, and there was a kind of olefin copolymer (Viscoplex-4-677) behaves the same of polyisobutylene where it can be used as drag reduction agent.

measurements of Mark-Houwink parameters (k and a) were done for polyisobutylene in crude oil equal to 0.0442 and 0.558 respectively and for gas oil equal to 0.0415 and 0.6 respectively at a temperature of 40°C and they are not determined in previous literatures .

It was noted that there are two types of polymers used as drag reduction agent, neutral polymers such as polyisobutylene, and other polyelectrolytes such as Xanthan Gum. It was found that polyelectrolyte has different behavior from

the neutral polymers, the reduced viscosity increases as concentration of polymer decreases.

It has been found that the addition of polyisobutylene to crude and gas oil decrease the flow activation energy of this fluids.

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Notations

Symbols	Notations	Units
A_1, A_2, A_3, A_4, A_5 and A_6	Constant in Equation 2.21	
A, b, c, d, e, h and g	Constant in Equation 2.23	
a	Mark-Houwink constant	
C	Concentration	g/cm^3
C_1 , C_2	Constant in W-L-F Equation	
E	Activation Energy for Flow	kJ/ mole
E_o	Flow Activation Energy of Solvent	kJ/mole
E_τ	Activation Energy for Flow at A constant Shear Stress	kJ/mole
E_{γ°	Activation Energy for Flow at A constant Shear Rate	kJ/mole
$\left(\Delta E_\gamma\right)_L$	Activation Energy for Flow at Low Temperature	kJ/mole
$\left(\Delta E_\gamma\right)_H$	Activation Energy for Flow at High Temperatures	kJ/mole
g	Constant in Equation 2.24	
K	Mark-Houwink constant	cm^3/g
k'	Huggins Constant	
k''	Kraemer Constant	
k'''	Suhulz-Blaschke Constant	
M	Molecular Weight	g/ mole

μ_s	Dynamic Viscosity at Temperature Ts	cP
m	Temperature Constant Above T_g	K
N_B	Number of Particles	
n	Number of Carbon Atoms in The chain	
n_B	Moles of Polymer	
Q	Unknown Proportionality Constant	
R	Universal Gas Constant	8.314J/mole .K
Tg	Glass Transition Temperature	K
T_S	Standard Reference Temperature	K
t_0	Flow Time of The Solvent	Secn.
t	Flow Time of The Polymer Solutions	Secn.
v_η	Hydrodynamic Volume of Each Sphere	
V	Total Volume	

Greek Letters

$[\eta]$	Intrinsic Viscosity	cm^3/g
η	Viscosity of Polymer Solution	cSt
η_o	Viscosity of Pure Solvent	cSt
η_r	Relative Viscosity	
η_{sp}	Specific Viscosity	
η_{red}	Reduced Viscosity	cm^3/g
εr	Dielectric Constant	
$t_g\ \delta$	Dissipation Factor	

μ	Dynamic Viscosity	cP

Subscripts

0	at Time=0
o	without Polymer Additives
r	Relative
sp	Specific
red	Reduced
τ	Shear Stress
γ°	Shear Rate

Abbreviations

API	American Petroleum Institute
AM	Acrylamide
CMC	Sodium Carboxymethylcellulose
CTAB	Cetyl Trimethyl Ammonium Bromide
CMO	Correlation of Molecular Orientations
CMG	Carboxymethyl Guar
DMC	Methacryloxyethyl Trimethylammoniumchloride
FAE	Flow Activation Energy
HEC	Hydroxyethylcellulose
IV	Intrinsic Viscosity
IAIV	Isoamyl Isovalerate
GG	Guar Gum
M.WT	Molecular Weight
OCP	Olefin Copolymer
PEO	Polyethyleneoxide
PAM	Polyacrylamide
PMMA	Polymethylmethacrylate
PS	Polystyrene
PDMS	Polydimethylsiloxane
PIB	Polyisobutylene
PCIP	Polycisisoprene
PP-1	Polypentene-1
PPmer	Polypentenamer

PDMS	Polydimethylsiloxane
PDLLA	Poly (DL-lactic acid)
PVC	Poly (viny1 chloride)
PPM	Part Per Million
VI	Viscosity-Index
XG	Xanthan Gum
W-L-F	Williams, Landel and Ferry

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Chapter One

Introduction

1.1 Crude Oil

Crude oil or petroleum is defined as a naturally occurring mixtures consisting predominantly of hydrocarbons and / or of sulphur, nitrogen and / or oxygen derivative of hydrocarbons, which is removed from the earth in a liquid state. Petroleum is commonly accomplished by varying quantities of extraneous substances such as water, inorganic matter, and gas. The removal of such extraneous substances alone does not change the status of the mixture as crude petroleum.

Physically, crude oil can vary from liquids, mobile, straw colored liquid containing a large proportion of easily distillable material to highly viscous, semisolid black substances from which very little material can be removed by distillation before the onset of thermal decomposition. Densities generally lie in the range 0.79 to 0.95 g/cm^3 under surface condition and viscosities vary widely, from about 0.7 centipoises to more than 42000 centipoises (1).

The chemical composition of crude oils is surprisingly uniform even though their physical characteristics vary widely. The hydrocarbons present in crude petroleum are classified into three general types: paraffins, naphthens, and aromatics. In addition, there is a fourth type, olefins, that is formed during processing by the dehydrogenation of paraffins and naphthenes (2).

because of the chemical structure of crude oil; long hydrocarbon molecules can be cracked or recombined into shorter molecules with different characteristics and it can refined into everything from tar, gas oil, diesel and jet fuel to heating oil and natural gas. It is also an ingredient, feedstock, for the manufacturing of chemicals, fertilizers, plastics, synthetic fibers, rubbers and others (3).

Additives are added to different solvent for different purposes for example, some polymers are used for lubricating oil in low concentration, to increase viscosity index, reduce pour point and others(4).

Other polymers are used to improve the flow behavior of the crude oil and other solvents, such as water for its transport through pipe lines (as drag reduction agent) (5).

Drag reduction(DR) phenomena had been well documented in which the fluid that containing these additives requires a lower pressure drop than pure solvent to maintain the same flow rate in a pipe. This behavior can offer large economic advantages and a larger effectiveness of the pipeline transportation (6-9).

These applications showed a higher ability of polymers in reducing drag and increasing oil flow rate without the need to any additional pumping stations or new pipelines (6).

Effective polymeric DR additives are considered to be flexible, linear with a high molecular weight such as polyisobutylene (10-11).

1.2 Intrinsic Viscosity

Intrinsic viscosity (IV) is a viscometric method for measuring molecular size, this means that intrinsic viscosity depends directly on chain dimensions of molecular. Intrinsic viscosity is based on the flow time of a polymer solution through a narrow capillary relative to the flow time of the pure solvent through the capillary. The unit of intrinsic viscosity is inverse concentration. Intrinsic viscosity is simple, inexpensive to obtain and reproducible between different laboratories (12, 13).

From our knowledge in intrinsic viscosity, the behavior of polymer could be known which is neutral or polyelectrolyte.

From intrinsic viscosity of different molecular weight, Mark-Howink parameters could be determined and used for unknown molecular weight for the same system.

1.3 Flow Activation Energy

Viscous flow in any liquid can be regarded as a thermally activated rate process where atoms, molecules, or groups of molecules (flow units) must overcome an energy barrier to move to an adjacent vacant site or "hole" (14). Then activation energy is a very important parameter determining the mechanism of optical transitions (15).

1.4 Purpose of The Present Work:

1- Estimation of the intrinsic viscosity for different polymers which are used in previous literature either as drag reduction agent or viscosity index improver in crude oil and other solvents.

2- From the intrinsic viscosity, The Mark-Houwink parameters were calculated for different molecular weights for polyisobutylene in crude and gas oil.

3- Determination of flow activation energy for polyisobutylene in crude and gas oil. Then, the effects of changing the molecular weight on it were studied.

Chapter Two

Literature Survey

2.1 Intrinsic Viscosity

Intrinsic viscosity $[\eta]$ may be regarded as a measured of the specific hydrodynamic volume of dissolved polymer in at infinite dilution $C \rightarrow 0$ (16). Intrinsic viscosity measured in specific solvent is related to molecular weight M, by the Mark –Houwink equation (17, 18).

$$[\eta] = KM^{a} \tag{2.1}$$

Where k and a are Mark-Houwink constant that depends upon the typed of polymer, solvent, and the temperature of the viscosity determinations (17) .The unit of intrinsic viscosity is inverse concentration (19).

A plot of the log $[\eta]$ vs. log M usually gives a straight line, the slope of this line is the "a" value and the intercept is equal to the log of the "k" value as shown in Fig. 2-1 (17)

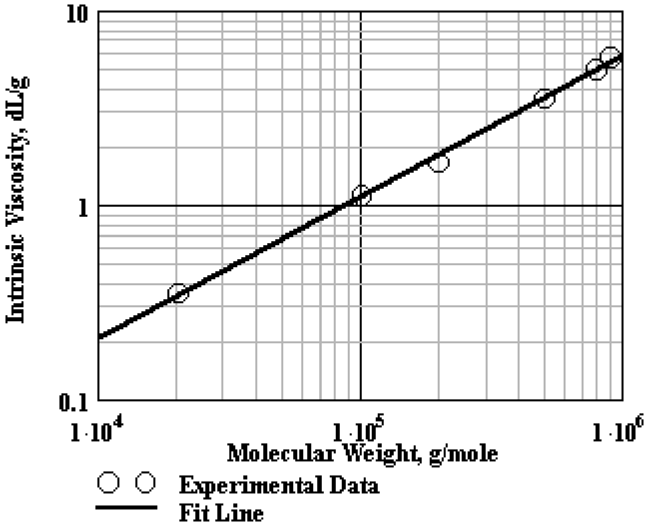


Figure 2-1 Logarithmic Plot of [η] vs. M (Schematic) (17)

The slope contains information about the shape of molecules, as illustrated below

- a= 1/2 (for flexible polymer chain in "ideal" solvent).
- 0.5<a<0.8(for flexible polymer chain in "good" solvent).
- a>0.8(for "stiff" chain) (19).

Where k and a values for some polymer/solvent system are given in table (2-1) (20, 21).

Table 2-1 Mark−Houwink Parameters for Various Polymers and Solvents (20, 21)

Polymer	Solvent	Temperature/^{o}C	k (cm^3/g)	a
Polyisobutylene	Benzene	30	0.061	0.56
	Toluene	30	0.02	0.67
	Cyclohexane	30	0.0276	0.69
	Carbon tetrachloride	30	0.029	0.68
Polymethylmethacrylate	Acetone	30	0.0077	0.7
	Acetonitrile	30	0.0393	0.5
	Benzene	30	0.0052	0.76
	Toluene	30	0.007	0.71
Polycisisoprene	Toluene	30	0.002	0.728
Polyacrylamide	Water	30	0.0373	0.66
Polydimethylsiloxane	Toluene	30	0.0215	0.65
Hydroxyethylecellulose	Water	30	0.00948	0.87
Polyethylene oxide	Water	30	0.00875	0.79
	Benzene	30	0.0397	0.686

The viscosity of a polymer solution (η) is higher than that (η_o) of the pure solvent at a specified temperature and the increase in medium viscosity on dissolving the polymer in the solvent is a function of both molecular weight and concentration of the polymer solute.

If the polymer solution is very dilute, then the viscosities of the solvent and the solution at a given temperature would be proportional to their flow times in a given capillary viscometer such that the relative viscosity η_r expressed by the ratio (η / η_o) would be given by the flow time ratio (t / t_o), where t_o is the flow time of a given volume of the solvent and t is the flow time of the same volume of solution respectively. The parameter called specific viscosity, η_{sp} as defined by $\eta_{sp} = (\eta - \eta_o) / \eta_o = (t - t_o) / t_o$, where specific viscosity per concentration equal to reduced viscosity, and intrinsic viscosity is :(22)

$$[\eta] = \lim_{c \to 0} \eta_{red} \tag{2.2}$$

The term of $[\eta]$ has been related to the three viscosity function through the following three equations by Huggins, Kraemer, and Suhulz-Blaschke respectively :(23, 24)

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c \tag{2.3}$$

$$\frac{(\ln \eta_{rel})}{c} = [\eta] - k''[\eta]^2 c \tag{2.4}$$

$$\frac{\eta_{sp}}{c} = [\eta] + k'''[\eta]\eta_{sp} \tag{2.5}$$

Where k' , k'' and k''' are constants for a given polymer – solvent – temperature systems. The value of $k' + k''$ has been shown to be 0.5 (20).

2.1.1 Relation of Intrinsic Viscosity with Molecular Weight

Enistein derived the specific viscosity for dilute solution of hard spheres as in equation below:

$$\eta_{sp} = 2.5\frac{N_B V_\eta}{V} \tag{2.6}$$

Where N_B is the number of particles (hard spheres), V_η is the hydrodynamic volume of each sphere, and V is the total volume. For a first approximation to polymer solutions, Einstein's Theory will be used and assumes each polymer to be a hard sphere with V_η equal to some effective hydrodynamic Volume. Letting moles of polymer be n_B = NB/L, then Equation (2.6) become:

$$\eta_{SP} = 2.5\frac{n_B V_\eta L}{V} \tag{2.7}$$

For a monodisperse polymer solution with concentration c = n_BM/V, where M is molecular weight, so that η_{sp} can be rewrite as:

$$\eta_{sp} = 2.5\frac{n_B M}{V}\frac{V_\eta L}{M} = 2.5c\frac{V_\eta L}{M} \tag{2.8}$$

$$\frac{\eta_{SP}}{c} = 2.5\frac{V_\eta L}{M} \tag{2.9}$$

This result is for an ideal solution. From these two equations it is clear that $\frac{\eta_{sp}}{c}$ in an ideal solution is independent of concentration. Extrapolating to zero concentration, which is trivial because $\frac{\eta_{sp}}{c}$ is independent of c, the intrinsic viscosity of an ideal solution is:

$$[\eta] = \lim_{c \to 0}\frac{\eta_{sp}}{c} = 2.5L\frac{V_\eta}{M} \tag{2.10}$$

For a hard sphere v_η could be taken to be the volume of that sphere or, equal to $4\pi r^3/3$. Because of the polymer is not a hard sphere; the result is not simple. It can, however, probably assume that v_η is being proportional to root-mean-squared radius cubed $\left(\sqrt{\langle r^2\rangle}\right)^3$. Writing Q for the as yet unknown proportionality constant, $V_\eta = Q\left(\sqrt{\langle r^2\rangle}\right)^3$.The proportionality constant was lumped along with other constants in the above equation and the results:

$$[\eta] = \phi \frac{\langle r^2\rangle^{3/2}}{M} = \phi \left(\frac{\langle r^2\rangle}{M}\right)^{3/2} M^{1/2} = \phi \left(\frac{\langle r^2\rangle_0}{M}\right)^{\frac{3}{2}} M^{\frac{1}{2}} \alpha^3 \qquad (2.11)$$

Where ϕ = 2.5LQ. In the last step of the above equation the root-mean-squared end-to-end distance is rewrote using the expansion factor α and the unperturbed end-to-end distance:

$$\langle r^2\rangle = \alpha^2 \langle r^2\rangle_0 \qquad (2.12)$$

In a theta solvent the expansion factor is 1 (α = 1) and the above equation shows that $[\eta]$ is proportional to the square root of molecule weight and the 3/2 power of $\langle r^2\rangle_0/M$

$$[\eta] = \phi \left(\frac{\langle r^2\rangle_0}{M}\right)^{3/2} M^{1/2} \qquad (2.13)$$

But, both $\langle r^2\rangle_0$ and M are proportional to the number of bonds or n. Thus $\langle r^2\rangle_0/M$ is a constant for a particular polymer that is independent of molecular weight. Then, the simplest form is

$$[\eta] = KM^{1/2} \qquad (2.14)$$

In other terms

$$[\eta] = KM^{a} \tag{2.15}$$

Where k and a are Mark-Houwink constant that depends on the polymer-solvent pair and on temperature (25, 26).

2.2 Additives

2.2.1 Polymers

The polymeric is added to hydrocarbon and other solvents used for different purposes, for example some polymers are used for lubricating oil to increase the viscosity index, and other polymers are used in reducing the energy requirement of crude oil or other solvent transportation through pipes.

The polymer are long chain molecules when added in dilute concentrations to fluids, they reduce friction drag in pipes by as much as 20 % – 80 % (27). Table 2-2 shows the types of polymers dissolved in solvent (28).

Table 2-2 Types of Polymers Dissolved in Solvent (28).

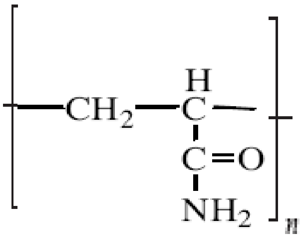
Water soluble	Hydrocarbon soluble
Polyethyleneoxide (PEO)	Polyethyloxide (PEO)
Polyacrylamide (PAM)	Polymethylmethacrylate (PMMA)
Sodium Carboxymethylcellulose (CMC)	Polystyrene (PS)
Guar Gum (GG)	Polydimethylsiloxane (PDMS)
Xanthan Gum (XG)	Polyisobutylene (PIB)
Hydroxyethylcellulose (HEC)	Polycisisoprene (PCIP)

Poly (ethylene oxide) (PEO) is completely soluble in water at room temperature. It is also soluble in several organic solvents, particularly chlorinated hydrocarbons. Aromatic hydrocarbons are better solvents for poly (ethylene oxide) at elevated temperatures. (PEO) is flexible, linear with high molecular weight, its utility in multiple pass application. The structure of (PEO) is shown below (29, 30)

$$(-CH_2-CH_2-O-)_n$$

Jeon and Chang, (31) the effect of temperature on the conformational properties of poly (ethylene oxide) (PEO) in aqueous and aqueous urea solutions. The values of intrinsic viscosity and Huggins coefficient for the PEO dissolved in water and urea/water mixtures (urea concentration 0.2, 1, and 2 M) were obtained using a viscometry method and discussed with respect to the change of water structure. At low temperature (below 22°C), the PEO-water interaction is favorable and the chain can be extended, whereas at higher temperature (above 24°C), it is less favorable and the chain can be contracted, i.e., the PEO-water interaction becomes to be unfavorable with the increase in temperature. As the urea is added to system, the PEO chain can be more extended and huged by the perturbation of the structured water originating from the unfavorable PEO-water interaction

Polyacrylamide (PAM) is Amorphous, high affinity for water and completely miscible in water, Low toxicity and Low cost. The structure of (PAM) is shown below (29, 32)



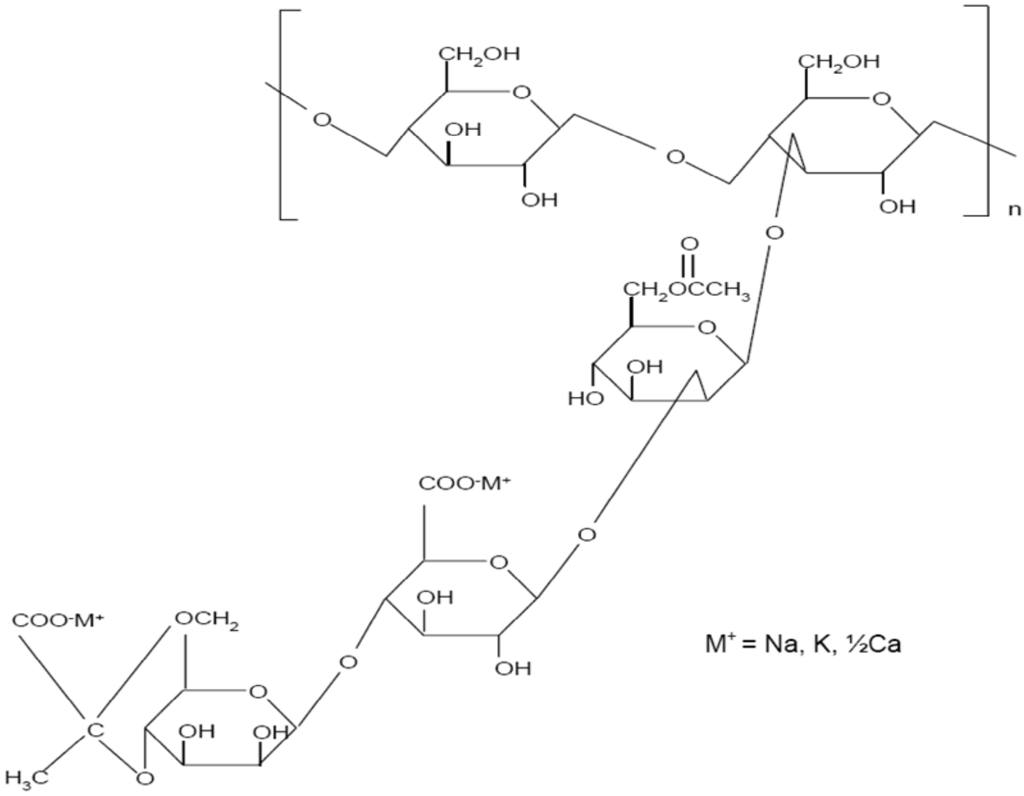
$$\left[-CH_2-\underset{\underset{NH_2}{|}}{\underset{C=O}{\underset{|}{\overset{H}{C}}}}-\right]_n$$

Xiaowu et al., (33) a novel cationic polyacrylamide modified with fluorinated acrylate had been synthesized of acrylamide (AM), methacryloxyethyl trimethylammoniumchloride (DMC), and 2-(perfluorooctyl)ethyl acrylate (FEA) by free radical micellar copolymerization in aqueous solution utilizing cetyl trimethylammonium bromide(CTAB) as the surfactant and potassium persulfate (KPS)/sodium bisulfite (SBS) as the redox initiator. Surface activity and flocculation of the polymer were studied. The results showed that with the incorporation of FEA, the intrinsic viscosity decreased until the modified polymer was not able to dissolve in water; and with the increase of CTAB and KPS, the intrinsic viscosity decreased firstly then increased slowly. The polymer exhibited good surface activity in both water and salt solution. The results demonstrated the superiority of the copolymer over the no-modified cationic polyacrylamide as a flocculant.

Xanthan gum (XG) is a natural polysaccharide produced by microorganism xanthomonas campestris. XG is a long chain polysaccharide composed of the sugars glucose, mannose, and glucuronic acid. The backbone is similar to cellulose with added side chains of trisacharides (three sugars in a chain). Xanthan is a white to cream colored free flowing powder soluble in both hot and cold water to give viscous solutions at low concentrations, but insoluble in most organic solvent (34-38). Its molecular weight is greater than 10^6 (38), as it is advantageous in industrial importance based upon its ability to control the rheology of water based systems. Even at low concentrations xanthan gum solutions show a high viscosity in comparison with other polysaccharide solutions. This property makes it a very effective thickener and stabilizer (35, 36, and 39).

XG has been used in a wide variety of food for a number of important reasons, including emulsion stabilization, temperature stability, and compatibility with food ingredients (41).

XG is used in pharmaceutical formulations, cosmetics, and agricultural products. High viscosity of solution and water solubility of polymer have created important application for xanthan in petroleum industry where it is commonly used in drilling fluids and in enhanced oil recovery processes (38, 40) .The structure of (XG) is shown below (35)



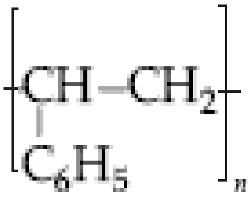
Khouryieh et al., (42) an oscillating capillary rheometer was used to investigate the effects of xanthan deacetylation on the viscoelastic properties and intrinsic viscosity of xanthan and guar mixtures in dilute aqueous solutions. Deacetylated xanthan exhibited a stronger synergistic interaction with guar than native xanthan due to the destabilized helical structure and increased chain flexibility of the deacetylated xanthan. No gels were observed for all xanthan–guar mixtures. Native xanthan–guar mixtures exhibited a liquid-like behavior, where as deacetylated xanthan–guar mixtures exhibited a gel-like behavior. The relative viscosity and elasticity of deacetylated xanthan–guar mixtures were much stronger than those for native xanthan–guar mixtures. The intrinsic viscosities of deacetylated xanthan–guar mixtures are higher than the calculated values assuming no interaction; whereas, the intrinsic viscosities of native xanthan–guar mixtures were lower than the calculated values assuming no interaction, demonstrating that intermolecular binding occurred between the disordered segments of xanthan and guar gum in dilute aqueous solutions.

Khouryieh et al., (43) an oscillating capillary rheometer was used to investigate the dynamic viscoelastic and intrinsic viscosity properties of deacetylated xanthan (0.025%), native xanthan (0.025%), guar gum (0.075%), and xanthan–guar mixtures in dilute solutions. Influence of ionic strength on xanthan conformation and interaction with guar gum was elaborated. In water and 2 mM NaCl solution, the relative viscosity and elasticity (η'')of both native xanthan–guar mixtures and deacetylated xanthan–guar mixtures were much higher than of those calculated for mixtures assuming no interaction, whereas no pronounced increase was found for polysaccharide mixtures in 40 mM NaCl. The intrinsic viscosities of deacetylated xanthan–guar mixtures in water and 2 mM NaCl were higher, whereas, the intrinsic viscosities of native xanthan–guar mixtures were lower than those calculated from the weight averages of the two individually, assuming no interaction. These results demonstrated that intermolecular interaction has occurred between xanthan and guar mixtures in water and 2 mM NaCl, but may not occur in 40 mM NaCl, and mutual incompatibility may occur. The results suggest that the degree of disordering of xanthan played a critical role in xanthan–guar interaction and may explain the differences in viscosity η, elasticity η'' and intrinsic viscosity measurements between 2 and 40 mM NaCl.

Polymethylmethacrylate (PMMA) is the synthetic polymer of methyl methacrylate. PMMA is thermoplastic that is hard and stiff but brittle. It has good abrasion and UV resistance and excellent optical clarity but poor low temperature. The structure of (PMMA) is shown below (44, 45)

$$[CH_2-C(CH_3)(COOCH_3)]_n$$

Polystyrene (PS) is Crystal clear thermoplastic, hard, rigid, free of odor and taste, ease of heat fabrication, thermal stability, low specific gravity, excellent thermal and electrical properties for insulating purpose, and low cost. (PS) is anionically polymerized polystyrene of a molecular weight about $1.5*10^6$. The suitable solvents for PS additive are pure chloroform, benzene and toluene. The structure of (Ps) is shown below (29, 46)

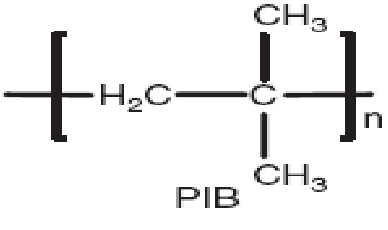


$$\left[-\underset{C_6H_5}{\underset{|}{CH}}-CH_2-\right]_n$$

Schmidt and Wolf, (47) the viscosity of dilute solutions of polystyrene in tert-butyl acetate was measured at temperatures ranging from 1.6 to 130°C and pressures up to 4000 bar by means of a rolling-ball viscometer. The present viscosity measurements show that the intrinsic viscosity assumes maximum values for variable pressure as well as for variable temperature.

Polyisobutylene (PIB) is usually classified as a synthetic rubber or elastomer, non–Newtonian fluid and as thixotropic liquids. PIB has unique properties: very low air, moisture and gas permeability, good thermal and oxidative stability, chemical resistance, and high tack in adhesive formulation (48, 49). PIB is colorless to light yellow, elastic, semisolid or viscous substance. It is odorless, tasteless, and nontoxic. PIBs are soluble in aliphatic and aromatic hydrocarbon solvents and insoluble in polar solvent. PIB is used in making adhesives, agricultural chemicals, fiber optic compounds, caulks and sealants, cling Film, paper and pulp, personal care products, and pigment concentrates, drag reducer and electrical insulation (49-51).

PIB of high molecular weight, such as Oppanol B types, control the viscosity index in lubricant oils. At ambient temperatures, lubricants have relatively high viscosity. At engine operating temperatures about 90 – 200 °C, the lubricants tend to lose a substantial amount of there viscosities. The addition of polymeric index improvers increases high temperature viscosity. At ambient temperature polymeric viscosity improvers tend to be tightly coiled into spherical bodies without substantial contribution to viscosity. As the temperature increases, the polymer tends to uncoil and become extended in solution. This extended more linear form increase viscosity in proportion to the degree of extension. Thus as the temperature increase the polymer contributes sufficient viscosity to the oil to maintain an adequate lubrication (52). The structure of PIB is shown below (49)



A physical property of PIB is shown in table 2-3 (49)

Table 2-3 Physical Properties of PIB That at are Independent of Molecular Weight

Density at 20°C	0.92 g/cm^3
Glass transition temperature, *T*g (differential scanning calorimetry)	−62°C
Specific heat	2 kJ·kg/K
Thermal coefficient of cubic expansion at 23°C	6.3×10^{-4} K^{-1}
Thermal conductivity	0.19 W/ K. m
Refractive index, *n*20D	1.51
Dielectric constant, εr (50 Hz, 23°C)	2.2
Dissipation factor, *tg* δ (50 Hz, 23°C)	≤5 × 10−4
Specific resistance	1.016 Ω·cm
Coefficient of permeability to water vapor	2.5 × 10−7 g /m·h·mbar

Fox et al., (53) intrinsic viscosity of polyisobutylene fractions covering a wide molecular weight range have been measured in cyclohexane, carbon tetrachloride, diisobutylene, toluene, and benzene at various temperatures from -10°C to 90°C. The intrinsic viscosity for a given polymer in different solvents at the same temperature decreases regularly from the best to the poorest solvents for the polymer. The intrinsic viscosity in the poorest solvents, benzene and toluene, increased rapidly with temperature. Log-Log plots of the intrinsic viscosity versus the molecular weight in a given solvent at a particular temperature are approximately linear over a wide molecular weight range; the slope of the line increases with increasing solvent power from 0.53 for benzene at 25°C to about 0.70 for the best solvents. The results have been compared with theoretical interpretation of intrinsic viscosity of high polymers. The dependence of the intrinsic viscosity on the molecular weight, solvent power, and temperature is in agreement with theoretical predictions.

Fox et al., (54) intrinsic viscosity of PIB fraction (M =$1.8*10^{5}$ to $1.88*10^{6}$) have been determined in various pure solvent and in several solvent mixture also, over wide temperature ranges. The results provide a rigorous test of the theory relating the intrinsic viscosity to polymer chain structure and to thermodynamic parameter governing the interaction between polymer and solvent. The parameter K in equation $[\eta]=KM^{1/2}\alpha^{3}$ is the same in different solvent, but decreases some what with temperature ($1.08*10^{-3}$ at 24°C to $0.91*10^{-3}$ at 105°C). Then, the temperature dependence of the intrinsic viscosity for PIB in wide variety of solvents is represented.

Nekrasova and Eskin, (55) measurement of the partial specific volume $\bar{v}$ and intrinsic viscosity $[\eta]$ of polyisobutylene in sixteen solvent has shown that $\bar{v}$ is dependent not only on the thermodynamic quality of the solvent, but also on its chemical structure. From constancy of $[\eta]$ of polyisobutylene in a number of n-alkanes (up to n-decane), it may be concluded that the difference between the entropic and enthalpic parameter of solution is proportional to (n+2.84), where n is the number of carbon atoms in the chain.

Fumiaki Abe et al.,(56) intrinsic viscosity was determined for 19 samples of oligo_ and polyisobutylene (PIB) in the weight average molecular weight, M, range, range from $1.12*10^{2}$ to $1.79*10^{6}$ in isoamyl isovalerate (IAIV) at 25°C and in benzene at 25°C. In the rang of M, the values of $[\eta]$ are definitely large in IATV than in benzene.

2.2.1.1 Review of Intrinsic Viscosity for Different Polymers

Bianchi and Peterlin, (57) experiment evidence concerning the dependence of the intrinsic viscosity $[\eta]$ on molecular weight M in the low molecular weight range(from oligomers to M = $5*10^4$) has been collected in a variety of solvent for about ten polymers. i.e., polyethylene, poly (ethylene oxide), poly (propylene oxide), polydimethylsiloxane, polyisobutylene, poly (vinylacetate), poly (methyl methacrylate), polystyrene, poly-α-methylstyrene, and some cellulose derivatives. the results showed the different in Mark-Houwink constant (a) of different polymer depends on : (1) variation of thermodynamic interaction with molecular weight; (2) variation of conformational characteristics (as for instance the ratio $\left\langle r_0^2 / nl^2 \right\rangle$, where $\left\langle r_0^2 \right\rangle$ is the unperturbed mean square end-to-end distance and n is the number of bonds each of length L; (3)hydrodynamic properties of short chains.

Filiatrault et al.,(58) intrinsic viscosities $[\eta]$ of four homopolymers: polyisobutylene (PIB), polypentene-1 (PP-l), Polypentenamer (PPmer), and polydimethylsiloxane (PDMS), and of an ethylene-propylene copolymer containing 81% ethylene (81% E) have been measured at 25°C in seven linear alkanes ranging from n-C6 to n-C16 and three highly branched alkanes, 2, 2, 4-trimethylpentane, 2, 2, 4, 6, 6-pentamethylheptane, and 2, 2, 4, 4, 6, 8, 8-heptamethylnonane**.** Correlation of molecular orientations (CMO) in the polymers was investigated. The difference $\Delta[\eta]$ is used as a test of CMO.

Nawaz,(59) the intrinsic viscosity, Huggin constant, Laser light scattering ,UV and IR measurement of nylon 6 are made in its solvent m-creosol and its mixture with different non-solvent like water, 1, 4-dioxane, m-cresol and 0.01N HCL. These measurements are also made at different temperatures (20-60°C). The variation in intrinsic viscosity, Huggin constant and other characteristics of the polymer solution with solvent composition and temperature are explained in terms of thermodynamic quality of solvent.

Lee and Tripathi, (60) a microchip-based method is developed for measurements of viscosity, intrinsic viscosity of polymer and biopolymer solutions. The measured values of intrinsic viscosity agree remarkably well with the available data obtained using different methods. The method offers a new way to study the conformational changes in proteins and DNA solutions in various buffer conditions such as pH, ionic strength, and surfactants.

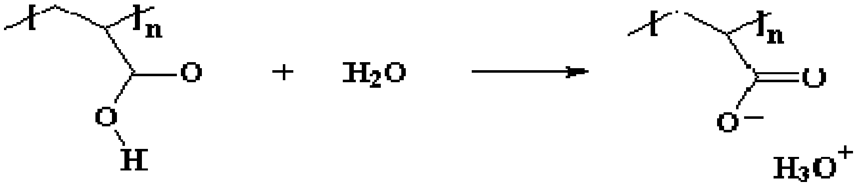
Lee and Kim, (61) the intrinsic viscosities were determined for poly (DL-lactic acid) (PDLLA) solutions in 1, 2-dialkyl phthalate at temperatures ranging from 30 to 60 °C. A series of dialkyl phthalate, in which the alkyl group was changed from methyl to propyl, was used as the solvent to control the solvent quality systematically. The intrinsic viscosity of the PDLLA solution was higher in the better quality solvent, with a higher molecular weight of PDLLA, and at lower temperatures. The unperturbed dimensions of the PDLLA molecule and polymer-solvent interaction parameter of PDLLA in dialkyl phthalate were deduced using extrapolation methods based on the temperature-dependent intrinsic viscosities. Slight shrinkage in the unperturbed chain dimension was observed, which resulted from a change in polymer conformation with temperature. It was also observed that the polymer-solvent interaction became more favorable with the dialkyl phthalate containing a shorter alkyl chain.

Pamies et al., (62) the determination of the intrinsic viscosity by single-point determinations, like that based on the Solomon–Ciuta equation, have been proposed as efficient alternatives to dilution procedures. With a basis on theoretical analysis and computer simulation, the systematic and global bias of the Solomon–Ciuta result were evaluated and showed how it depends on the strength of the concentration dependence of the solution viscosity (represented by the intrinsic viscosity and the Huggins constant) and the concentration of the single measured solution. It is proposed that an estimated Huggins constant can be employed in a corrected Solomon–Ciuta procedure, which may yield results for the intrinsic viscosity that are even more accurate than those from the Huggins extrapolation. This gives support and utility to the use of the single-point procedure when the intrinsic viscosity has to be determined for a unique concentration. It is also pinpointed specific circumstances where the dilution–extrapolation procedures should be preferred.

Omran, (63) This investigation covers a study on the effect of additives on the intrinsic viscosity of basic lubricating oils. The three types of Iraqi base lube oil-stocks, namely 40 stocks, 60 stocks, 150 stocks were mixed with additives. The three types of additives from olefin copolymer (OCP_1, OCP_2, OCP_3) were used and one type of poly alkylmathacrylates (PAMA). Usually the dynamic viscosity decreases with increasing the temperature. Additives were used to improve the viscosity index. This investigation studies the effect of the temperature change and the concentration (weight percent) on the intrinsic viscosity and Huggins constant of different type of mixtures, such as binary mixture and multi-component mixtures. This investigation and the results of experimental work recommend the best polymer additive for the selected based-oils.

2.2.2 Polyelectrolyte

Some of polymers are polyelectrolyte. Polyelectrolytes are polymers whose repeating unit bears an electrolyte group. These groups dissociate in aqueous solutions, making the polymers charged(64, 65), other terms Polyelectrolyte are polymers that fall apart in polar solvent for examples polyacrylic acid Put in water and the acid hydrogens split off with the water molecules and form H_3O^+ ions, as shown below (66):



The polymer is left with bunch of negative charged groups; all those negative charges are going to repel each other. Polyelectrolyte can be divided into ‘’weak‘‘ and ‘‘strong‘‘ types. A strong polyelectrolyte is one which dissociates completely in solution for most reasonable pH values. Weak polyelectrolyte will be partially dissociated at intermediate pH. Thus, weak polyelectrolytes are not fully charged in solution, and moreover their fraction charge can be modified by changing the solution pH, counterion concentration, or ionic strength (64, 69). The dilution of polyelectrolyte solution with the fixed ionic strength solvent, the counterions is diluted so that the net ionic strength of the solution decreases as dilution increases. The effect of decreasing ionic strength, as is well known, is to increase the polyelectrolyte coil dimensions by the electrostatic repulsion between its charged groups. Most likely the due to coil expansion, the hydrodynamic volume fraction of the polyelectrolyte in solution increases even as the mass concentration decreases and this effect on the configuration manifest itself in a very large intrinsic viscosity (67, 21).

2.2.2.1 Application of Polyelectrolyte :

Polyelectrolytes have many applications, mostly related to modifying flow and stability properties of aqueous solution and gels. They can also used to impart a surface charge to neutral particles, enabling them to be dispersed in aqueous solution. They are thus often as thickeners, emulsifiers, conditioners, flocculants, and even drag reducers. They are used in water treatment and for oil recovery. Many soups, shampoos and cosmetic incorporate polyelectrolyte. Additionally, they are added to many foods. Finally, they are used in a variety of materials, including cement. Because some of them are water-soluble, they are also investigated for biochemical and medical applications. There are currently much research in using biocompatible polyelectrolyte for implant coatings, for controlled drug release, and other applications (64, 65).

2.2.2.2 Review of Intrinsic Viscosity of Polyelectrolyte

Antonietti et al.,(70) a set of critically cross linked polystyrenesulfonates with fractal geometry having molecular weights in the range $4.96 * 10^5 < M < 3.07 * 10^6$ was prepared and characterized by viscometry in salt free aqueous solutions. Also these structures show the polyelectrolyte effect, which is a strong increase in reduced viscosity with decreasing concentration.

Rushing and Hester, (71) a new relationship based on Yamakawa-Fujii and OSF theories was developed to describe the contribution of electrostatic forces to the excluded volume of a polyelectrolyte in solution. The model is valid for flexible polymer coils in aqueous salt solutions where intermolecular interactions are minimal. A new dimensionless parameter group termed the dimensionless viscosity was shown to be related to the commonly expressed dimensionless ratio of solution screening length to polyion charge spacing and the degree of polymerization. The model has been applied to intrinsic viscosity data reported in the scientific literature and data collected in the laboratory, all using sodium chloride solution ranging in ionic strength. The result is a model equation that appears to be universal for the polyelectrolytes studied here. It would be interesting to analyze data for additional polyelectrolyte–solvent systems to test the treatment further. Particularly, viscous properties measured for a polyelectrolyte in a non-aqueous solvent having bulk dielectric properties different from water should be considered.

Zeynali et al., (72) partially hydrolyzed polyacrylamide was prepared by free radical copolymerization in solution. The intrinsic viscosity has been determined by extrapolating the reduced viscosity to zero concentration. The effects of solvent, salt type and concentration, degree of hydrolysis, and polymer concentration on viscosity have been investigated. It was shown that the reduced viscosity of salt-free solution of partially hydrolyzed polyacrylamide as a result of polymer chain expansion increases with decreasing polymer concentration. In fact the polymer behaves like a polyelectrolyte in salt-free solution. Adding low molecular weight electrolyte to the polymer solution eliminates the polyelectrolyte effect and polymer behaves like a neutral macromolecule. The viscosity increases with increasing polymer concentration, which is usually observed in neutral polymers. The effect of dielectric constant on reduced viscosity was studied by varying the solvent type and concentration.

Pavlov et al., (73) comparative analysis of the methods for determination of the intrinsic viscosity of both neutral and polyelectrolyte molecules is made.

Wolf, (74) the linear extrapolation of $(\eta - \eta_\circ)/(\eta_\circ c)$ towards $C \rightarrow 0$ constitutes the basis of traditional methods to determine intrinsic viscosity, where η is the viscosity of polymer solutions of concentration c and $\eta_\circ$ is the viscosity of pure solvent. With uncharged macromolecules this procedure works well; for polyelectrolytes it fails because of the pronounced non-linearity of the above dependence of high dilution resulting from the increasing electostatic interactions. This contribution presents a new method for the determination of $[\eta]$. It rests upon the application of the laws of phenomenological thermodynamics to the viscosity of polymer solutions and introduces a generalized intrinsic viscosity enabling a comparison of differently charged and uncharged polymers.

Eckelt et al., (75) intrinsic viscosity was determined at 25°C for 10 samples of narrowly distributed sodium polystyrene sulfonate (the molecular weights M ranging from 0.9 to 1000 kg/mol) in pure water and in aqueous solutions containing 0.9wt% NaCl from the slope of $\ln \eta_{rel}$ versus polymer concentration. In the middle range of M, the $[\eta]$ values are in the former case almost 2 orders of magnitude larger than in the latter case. In the absence of salt, the plot of log $[\eta]$ as a function of log M exhibits a sigmoidal shape, which can be approximated within the interval 3< M(in kg mol^{-1}) < 30 by $\log[\eta] = -0.17 + 2.1 \log M$ .In the presence of salt, the following relation holds true in the entire regime: $\log[\eta] = -0.13 + 0.86 \log M$.

Badiger et al., (76) intrinsic viscosities were determined for solutions of carboxymethyl guar (CMG) in pure water and 0.9 wt% aqueous NaCl. To avoid the 0/0-type extrapolation typical for Huggins plots, a new procedure was used. For CMG and pure water, this requires only two adjustable parameters: the specific hydrodynamic volume of the polymer in the limit of infinite dilution and a hydrodynamic interaction parameter. The intrinsic viscosity of CMG (no salt) at room temperature is 6050 mL.g-^{1}; approximately half as large as that of Na- polystyrene sulfonate (Na-PSS) of comparable molar mass. The ratio of the intrinsic viscosities with and without salt is = 7 for CMG, as compared to >100 for Na-PSS. The reasons for the different behaviors of the two types of polyelectrolytes are being discussed.

2.3 Flow Activation Energy (FAE)

Viscous flow in any liquid can be regarded as a thermally activated rate process where atoms, molecules, or groups of molecules (flow units) must overcome an energy barrier to move to an adjacent vacant site or "hole". (14) When a liquid flows, layers of liquid molecules slide over each other, where intermolecular forces oppose the motion and cause resistance to flow. As temperature increases, the thermal energy of molecules increases and the vacant site or holes in the liquid increased. Henry Eyring modeled the concept of an activation energy barrier to flow (77). Activation energy is a very important parameter determining the mechanism of optical transitions (15).

Then the flow behavior of polymers is frequently characterized in terms of their viscosity's-temperature relationship (78). Presently, there are two commonly used expressions to evaluate the temperature dependency of the viscosity - one based on free-volume concepts, namely the equation proposed by Williams, Landel and Ferry (W-L-F), this equation is found to be approximately applicable to all polymers in a temperature range between Tg and Tg + 100 K. and the second, of the Arrhenius type, based on the absolute theory of rate processes as derived by Eyring, this equation is suitable at temperatures far above the glass transition temperature or the melting point for crystalline polymers (79-81).

W-L-F equation

$$\log\frac{\mu}{\mu_s}=\frac{C_1(T-T_S)}{C_2+(T-T_S)} \qquad (2.16)$$

Where μ and μ_s are the viscosity at temperature T and T_S, respectively; C_1 and C_2 are constants; and T_S is the standard reference temperature taken as Tg+50 K, where Tg is the glass transition temperature(79).

Modification of equation (2.16) using different constants and different characteristic temperatures has been proposed. But since Tg is a practical and easily available parameter, (2.16) is used preferentially (79).

Arrhenius-Eyring equation

$$\mu = A\exp\left(\frac{E}{RT}\right) \tag{2.17}$$

Where μ is the viscosity in cp at temperature T, T is temperature in K, A is a constant, E is the activation energy for flow in unit J/mole, and R is the universal gas constant (8.314 J/mole .K) (77, 80, 82).

For all systems, equation (2.17) would then provide a valid and useful means of predicting the viscosity-temperature dependence. It is more useful to rewrite equation (2.17)

$$\ln \mu = \left(\frac{E}{RT}\right) + \ln A \tag{2.18}$$

A plot of $\ln \mu$ versus (1/T) gives a straight line with a slope of E/R (77).

However, since polymers are non-Newtonian materials; their viscosity at fixed temperature is dependent on shearing stress or shearing rate. Thus, in the non-Newtonian region of polymer flow, a clear differentiation between E at a constant shear stress and E at a constant shear rate must be done. Thus (79):

$$E_\tau = R\left[\frac{\ln \mu}{(1/T)}\right]_\tau \tag{2.19}$$

$$E_{\gamma^\circ} = R\left[\frac{\ln \mu}{(1/T)}\right]_{\gamma^\circ} \tag{2.20}$$

Where E_{τ} , E_{γ° is activation energy for flow at a constant shear stress and at a constant shear rate respectively.

2.3.1 Review of Flow Activation Energy

Hopkins et al., (83) the relationship proposed by Ferry and his co-workers for the effects of frequency and temperature on the dynamic properties of certain polymers is shown to lead to a method for calculating the activation energy of viscous flow from relaxation, creep, and dynamic test data, the result agreeing with those obtained in steady-state flow.

Collins and Krier, (78) the melt rheology of poly (viny1 chloride) (PVC) resin has been investigated as a function of shear rate over an 80°C temperature range. The microcrystalline nature of PVC has been observed in the form of low activation energy $\left(\Delta E_{\gamma}\right)_L$ at low temperature and high activation energy $\left(\Delta E_{\gamma}\right)_H$ at high temperatures. The two distinct flow activation energies suggest different rheological flow units in the low and high temperature regions.

Quadrat and Bohdanecky,(84) used equations which describe the concentration dependence of the specific viscosity of polymer solutions and the temperature dependence of intrinsic viscosity and of the Huggins viscosity parameter, conditions were sought for which solution viscosity increases with temperature (flow activation energy is negative).

Saini and Shenoy,(80) a method based on the melt flow index rather than the conventional zero shear viscosity is suggested to estimate the activation energy for viscous flow of polymer melts. The method is particularly attractive due to its simplicity and because all the conditions for its derivation fit rather well within the validity range of applicability of the Arrhenius-type equation relating viscosity and temperature.

Munari et al., (85) poly (butyleneterephthalate) (PBTP) samples of different molecular weights, both linear and branched, were synthesized by mass polymerization and studied in the molten state with a melt-flow index apparatus at different temperatures in the range 245-27 °C. In the experimental conditions ($\gamma^{\circ} \leq$ 20s^{-1}) the behavior of PBTP samples was Newtonian. The flow activation energy E was found to increase with degree of branching: typically E was about 47 and 63-79 kJ/mol for linear and branched polymers respectively.

Maderek and Wolf, (86) poly (n-decyl methacrylate), a statistical copolymer of ethylene and propylene, and a diblock copolymer of styrene and hydrogenated butadiene were studied as representatives of various kinds of viscosity-index (VI) improvers. By means of viscosity measurements in the temperature interval from 37.8 to98.9°C up to a concentration of typically 1wt.-% polymer, the viscosity indices of the different systems and the corresponding intrinsic viscosities, Huggins coefficients, and activation energies of flow, E, were determined. The discussion of the obtained experimental material demonstrates that the VI of a base-oil can be raised in two clearly distinguishable ways: (i) via an increase in the viscosity due to the mere presence of the polymer and (ii) less general, via an additional reduction of E as a consequence of thermodynamic interactions.

Porter, (87) the present literature draws attention to correlations that can express the flow activation energy E in terms of the volume expansion coefficient (a) in the melt state and glass transition temperature T_g for linear polymers. From equation $E = \left(R/a \right)(T_g + m)^2 / (0.23T_g + m)^2$ where m is the temperature constant above T_g, predicts the E for polymers at temperature in range of T_g+ 150. This equation is found to give a good fit to data for a wide range of polymer compositions.

Abdul kareem, (88) the dynamic viscosity of Iraqi crude oils of different origins, are measured over a temperature range of 20-50°C with and without the addition reducing agent (DRA). The flow activation energy of crude oils is calculated using the viscosity measurement data.

A method is based upon API gravity at 298K, pour point of each crude oil and concentration of drag reducing agent (DRA) is developed to predict the flow activation of crude oil as follows:

$$E= A_1+A_2x\ (API/T_P)^{A3}+A_4X\ (API/\ T_P)^2+A_5XPPm+A_6X\ T_P \qquad (2.21)$$

Where:

A_1, A_2, A_3, A_4, A_5 and A_6 are constant, T_P is characteristic time

The predict activation energy is used to calculate the viscosity of crude oil using a three parameter equation of the following form:

$$\mu = A\exp^{\left(B/T\right)} \qquad (2.22)$$

$$A=a+b.API+C.API^2 +d.\ T_p+e.(API/T_p)+h(API/\ T_p)^2 \qquad (2.23)$$

$$B= g.\ E \qquad (2.24)$$

Where

a, b, c, d, e, h and g constants.

E= flow activation energy

The proposed correlations have been found to fit all experimental data consisting of 144 measurements, with an overall average absolute deviation error 6.62% for the flow activation energy and 3.2% for the viscosity equation.

Chen et al., (15) in this work, an accurate method for the measurement of activation energy was presented. They found that with increasing temperature, there is a step transition from one emission mechanism to another. This step transition gives us an accurate measurement of activation energy.

Nair, (89) nylon 6 (PA 6) is blended with polystyrene (PS), so as to reduce the moisture absorption and hence to impart dimensional stability to the polymer. The results show the study of the effect of temperature on the blends, the activation energy of the system has been calculated. The system exhibits relatively high activation energy at 50/50 composition.

Vyazovkin and Sbirrazzuoli, (90) the advanced isoconversional method provides a sound way of estimating the effective Activation energy, E for non-isothermal crystallization of the polymer melts. The experimentally obtained E dependence adequately reflects the changes in the crystallization kinetics that occur with changing the temperature of the process.

Salomon and Zhai, (77) the temperature dependence of viscosity of neat and modified asphalt binders were evaluated between 80 °C and 200 °C using rotational viscometry. The activation energy for flow was determined for these asphalt binders using the Arrhenius equation. Different types of polymer and polymer contents were selected to study the effects of polymer type and concentration on the activation energy for flow. Attempts were made to use a global model to evaluate the relationship between polymer content and viscosity. The results indicate that the flow activation energy can be used to rank the temperature susceptibility of different asphalt binders.

Chapter Three

Experimental Work

3.1 Materials

3.1.1 Solvents

In the present work, crude oil, gas oil and tap water were used as solvents. Crude oil and gas oil obtained from Al-Dura refinery. The properties of crude oil obtained from Al-Dura refinery are listed in Table 3-1

Table 3-1 Properties of Crude Oil (98)

Properties	magnitude
API	32.5
Salt	9.2 ppm
Pour point	Below -30°C
R.V.P	0.55 kg/cm^2
Water and sedimentation	0.05
Specific gravity	0.8633
Density	0.8662 g/cm^3

The general properties of gas oil obtained from Al-Dura refinery are listed in Table 3-2

Table 3-2 Properties of Gas Oil (98)

properties	magnitude
API	40
Initial boiling	158°C
End point	365°C
Flash point	62°C

The properties of tap water are shown in table 3-3

Table 3-3 properties of Tap Water

properties	(PPM)
Calcium	21.00
Magnesium	4.50
sodium	20.00
iron	0.01
Total dissolved salts	133
Total hardness as $CaCo_3$	80
pH	7.20

3.1.2 Additives

The hydrocarbon soluble additive such as polyisobutylene of types Oppanol B150, 200, and 250 of different molecular weights $2.5*10^6$, $4.1*10^6$, and $5.9*10^6$ g/mole, respectively, were acquired from BASF Company, Germany, this molecular weight of polyisobutylene was used because it has higher molecular weight and it is better as drag reduction agent than of low molecular weight, and also it is the only molecular weight was found. In addition with three types of additives, which were brought from Al-Dura refinery, They are olefin copolymer (OCP), {viscoples-4-677, viscoplex-215496, and Lubrizol R 7077}, copolymer which means polymer composed of two or more different monomer(91), olefin copolymers are copolymer of unknown structures, different companies are producing them. The water soluble additive is Xanthan Gum (XG) of molecular weight $3.7*10^6$ which was supplied from local market in Baghdad, and polyacrylamid (PAM) of high molecular weight. PAM was of unknown molecular weight and it was used because it is the only type available in local market in Baghdad.

All polymers were used in present work because they were used as drag reduction agent in previous literature (92, 93, 94, 95, 96), so that these polymers were studied to find their intrinsic viscosity and flow activation energy.

3.2 Dissolving Process

The dissolving of polymers was carried out in a magnetic stirrer, of type Heidolph, MR 3000, made in Germany, at room temperature. The method of dilute solution preparation takes 1 gram of polymer per 100 ml (w/v) of solvent in a conical flask. The magnetic stirrer was started at a speed of 500 rpm and increase continuously. A homogenous solution was obtained as show in Table 3-4

Table 3-4 Dissolving Times of Polymers Solution at Concentration (1g/100ml)

NO.	**polymers**	**solvents**	**DISSOLVING TIME**
1	Oppanol B 150	Crude oil	6 days
2	Oppanol B 200	Crude oil	7 days
3	Oppanol B 250	Crude oil	9 days
4	Viscoplex-4-677	Crude oil	2 hours
5	Viscoplex-215496	Crude oil	2 hours
6	Lubrizol R 7077	Crude oil	2 hours
7	Oppanol B 150	Gas oil	15 hours
8	Oppanol B 200	Gas oil	19 hours
9	Oppanol B 250	Gas oil	30 hours
10	Xanthan Gum(XG)	Water	6 days
11	Polyacrylamide(PAM)	water	3 days

Then, the homogeneous solution was diluted to different concentrations such as (0.5, 0.4, 0.3, 0.2, and 0.1g) per 100 ml of solvent (w/v) by the same magnetic stirrer for 30 sec. The dissolving of polymer solution is shown in Figure 3-1:

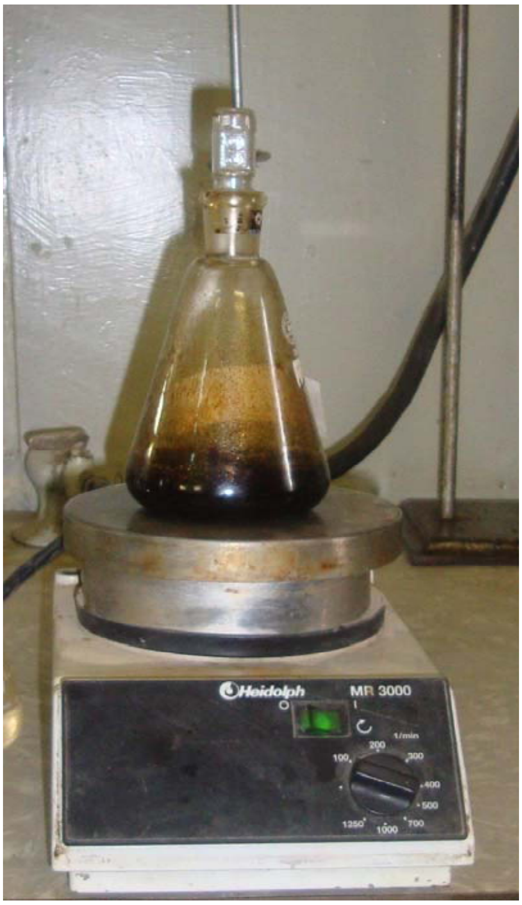


Figure 3-1 Magnetic Stirrer

The method of the concentrated solution preparation is the same as for diluted solution, it takes 2 gram of polymer per 100 ml (w/v) of solvent in a conical flask and then diluted to 1 and 0.5g/100ml (w/v) by magnetic stirrer for 30 sec only, but the time of dissolving 2g/100ml is higher than 1g/100ml.

3.3 Operating Procedure

a) For Dilute Solution Viscosity Measurement:

1. Prepare the pure solvent and different polymer solution to form dilute solution of concentration c_i such that:

C_1=0. 5 g/100ml

C_2=0. 4 g/100ml

C_3=0. 3g/100ml

C_4=0. 2g/100ml

The concentrations (0.5, 5.4, 0.3 and 0.2) were used in present work depending on previous literature (54), and because it found that these concentrations have many industrial applications.

2. The water bath has been prepared for low temperature measurements (40°C) and the oil bath for high temperature measurement (100°C), these temperatures were the only temperatures used in the present work because the operation of water bath and oil bath were limited to these temperatures in the laboratory of Al-Dura refinery, Figures 3-2 and 3-3 shown the water and oil bath, respectively.

Figure 3-2 Water bath

Figure 3-3 Oil bath

3. Ubbelhode viscometer (shown in Figure 3-4) was used to measure the flow time of the solvent (t_0) and flow time of polymers solutions (t).

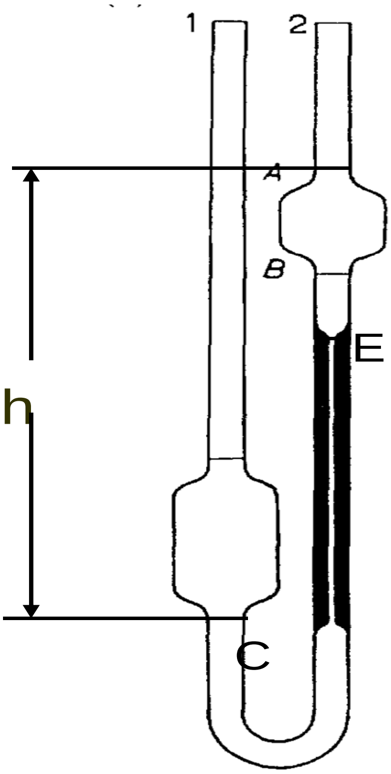


Figure 3-4 Ubbelohde Capillary Viscometer

Using The Ubbelohde Capillary Viscometer

This method is used for dilute solutions. Ubblehode viscometer has been used of different size. The procedure is as follows:

- The viscometer was cleaned using suitable solvents (water or benzene) and then dried by passing clean dry air to remove the final traces of solvents.
- The solution is placed in capillary viscometer (about 15ml).
- The viscometer is placed into the holder, and inserted to the constant temperature bath, (40 or 100°C).
- The solution was allowed approximately 10-15 minutes to come to bath temperature and become free of air bubbles.

- The solution was pulled above point A and the time calculated when the solution at point A until it reaches point B (using stop watch). The liquid flow through the capillary viscometer or narrow diameter section of viscometer because of the height different between C and A (h); there is hydrostatic head or driving pressure.
- The flow times and concentrations are used to calculated the intrinsic viscosity for solutions.

The time required for the solutions (solvent with additives) to flow from point A to point B is greater than of the solvent. If the flow occurs rapidly (t is small), the liquid is moving fast and kinetic energy will be significant. In this case it is important to correct the kinetic energy.

b) For Concentrated Solution Viscosity Measurement

1. The pure solvent and different polymer solution have been prepared to form concentrated solutions of concentration c_i such that:

C_1=2 g/100ml

C_2=1g/100ml

C_3=0.5g/100ml

2-The water bath was prepared for different temperatures (30, 40, 50, 60, and 70 °C) to measure the flow activation energy.

3- The rotational viscometer (Brookfiled DV-E), Figure 3-5, has been used which is measured the concentrated fluid viscosity at a given shear rate.

Figure 3-5 DV-E Viscometers

Using the DV-E Viscometer

This method is used for concentrated solution. In the present work the DV_E viscometer has been used. The principle of operation of the DV_E viscometer is to rotate the spindle. The viscosity measurements of DV_E viscometer is in centipoises or mille Pascal seconds. The viscometer was set in either speed or spindle select mode. When the set is in the left position, the operator may select speed of rotation. When the set is in the right position the operator may select spindle. The DV_E viscometers are provided with a set of four spindles. Each spindle must have entry code number to calculate viscosity value. The viscometer memory contains parameters for all spindles and the digits of each entry code for each spindle are listed in Table 3-5.

Table 3-5 Code of spindles for DV_E Viscometer

Spindle	LV_1	LV_2	LV_3	LV_4
Code	61	62	63	64

There are 18 rotational speeds available on DV_E viscometer, with range 0.3- 100 rpm .The procedure of measurement of the flow activation energy is as follows:

- The temperature of system was kept constant at 30°C and then changed to other temperatures.
- The thermometer was placed to check the temperature of solution.
- The DV-E viscometer has been prepared at constant shear rate (speed) as 100 rpm.
- The suitable code of spindle was selected for the sample.
- A small amount of solution was placed in a beaker. The solution is at the immersion limit on the spindle. As shown in figure 3-6

Figure 3-6 The DV-E Viscometer with Samples

- The viscosity was measured with each temperature (at constant shear rate) to get the flow activation energy for the solvent and solution.

Figures 3-4 and 3-5 show that there are two types of viscometers, one type is capillary viscometer which is used for Newtonian and diluted solution, and the second type is the rotational viscometer which is used for non-Newtonian and concentrated solution.

3.4 Calculations

a) Capillary Viscometer Measurements

1- The times of the solvent (t_0) and solution (t) was measured.

2- The relative viscosity was measured from $\eta_{rel} = t/t_0$.

3- The specific viscosity was calculated from $\eta_{sp} = \frac{t - t_0}{t_0}$.

4- The reduced viscosity was also calculated $\eta_{red} = \frac{\eta_{sp}}{c}$.

5- The $\eta_{red} = \frac{\eta_{sp}}{c}$ was plotted with each concentration to get intrinsic Viscosity $[\eta]$ as shown in figure 3-7

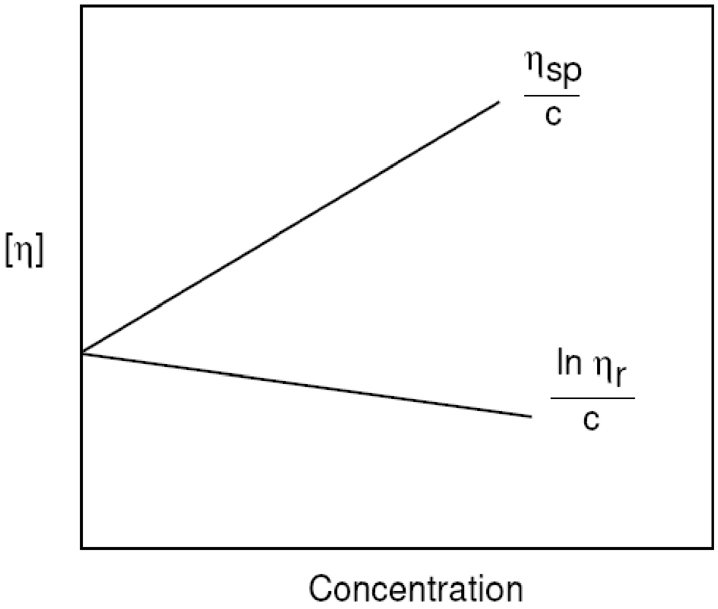


Figure 3-7 $\frac{\eta_{sp}}{c}$ or $\frac{\ln \eta_r}{c}$ Versus Concentration

b) Rotational Viscometer Measurements

1- The viscosity has been measured for each temperature for the solution at constant concentration and at given shear rate.

2- The Arrhenius-Erying equation (2.17) was used, and the $\log \eta$ was plotted with 1/T to get a straight line and the slope of the line was calculated, the flow activation energy, E, was obtained by multiplying the slope of the line by (2.303*R), where R is universal gas constant and equal to 8.314 J/ mole.K.

Chapter Four

Results and Discussions

4.1 Introduction

The present work deals with intrinsic viscosity $[\eta]$, Mark-Howink constants, and flow activation energy (FAE) for different polymers. The polymers were Polyisobutylene at different molecular weights, Xanthan Gum, Polyacrylamide, and different types of Olefin copolymer (OCP) dissolved in different solvents.

4.2 Intrinsic Viscosity of Additives Added to Crude Oil

The relative, specific and reduced viscosities were measured using Ubbelohde capillary viscometer to estimate the intrinsic viscosity for polyisobutylene at different molecular weights, and for olefin copolymer at two temperatures (40 and 100 °C).

4.2.1 Intrinsic Viscosity of Polyisobutylene in Crude Oil

Polyisobutylene, Oppanol B type with three different molecular weights, $2.5*10^6$ g/mole for Oppanol 150, $4.1*10^6$ for Oppanol 200 and $5.9*10^6$ for Oppanol 250, dissolved in crude oil by magnetic stirrer. The time of dissolving 1grams per 100 ml of crude oil (w/v), of Oppanol B 150 takes 6 days, Oppanol B 200 takes 7 days, and Oppanol B 250 takes 9 days and then diluted to different concentration for 30 seconds.

- Oppanol B 150, B 200 and B 250 were dissolved in crude oil; and the effect of concentration on reduced viscosity is represented graphically for two temperatures (40 and 100°C) as shown in Figures 4-1, and 4-2 respectively, and the results shown in tables 4-1, 4-2, A-1, A-2 , A-3, A-4, A-5 and A-6 in Appendix A.

Table 4.1 Reduced Viscosity of Crude Oil with Different Oppanol B at temperature 40 °C

Conc.(w/v)	$\eta_{red} = \eta_{sp}/conc.(100ml/g)$		
	B 150	B 200	B 250
0.5g/100ml	2.24	2.58	3.9
0.4g/100ml	2.2	2.5	3.72
0.3g/100ml	2.1	2.41	3.46
0.2g/100ml	2	2.35	3.33

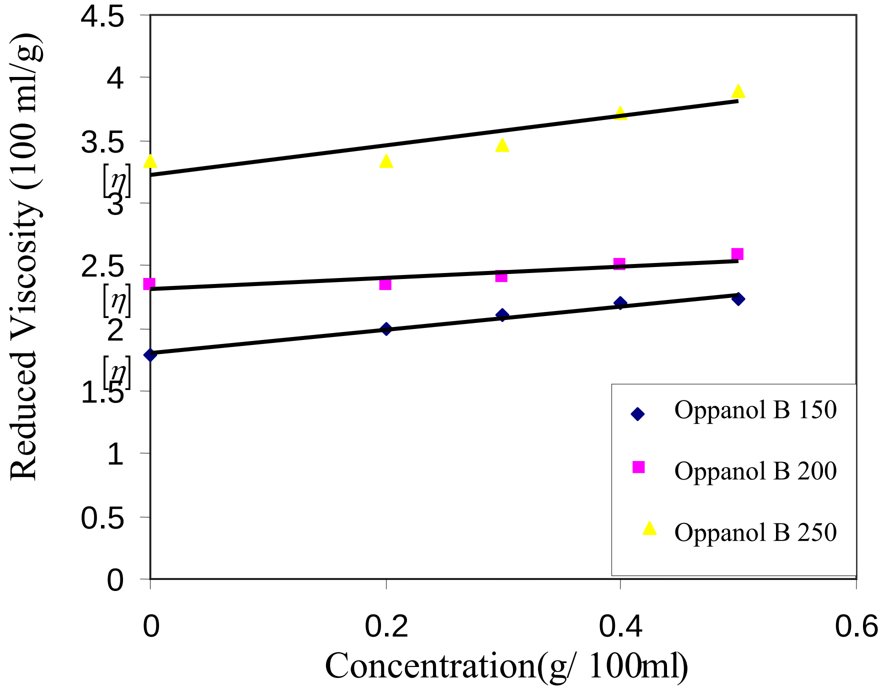


Figure 4-1 Reduced Viscosity Versus Concentration for Different Oppanol B in Crude Oil at Temperature 40°C.

Table 4-2 Reduced Viscosity of Crude Oil with Different Oppanol B at Temperature 100°C

Conc.(w/v)	$\eta_{red} = \eta_{sp}/conc.(100ml/g)$		
	B 150	B 200	B 250
0.5g/100ml	2.58	2.66	4.95
0.4g/100ml	2.36	2.55	4.44
0.3g/100ml	2.15	2.43	4
0.2g/100ml	1.93	2.32	3.58

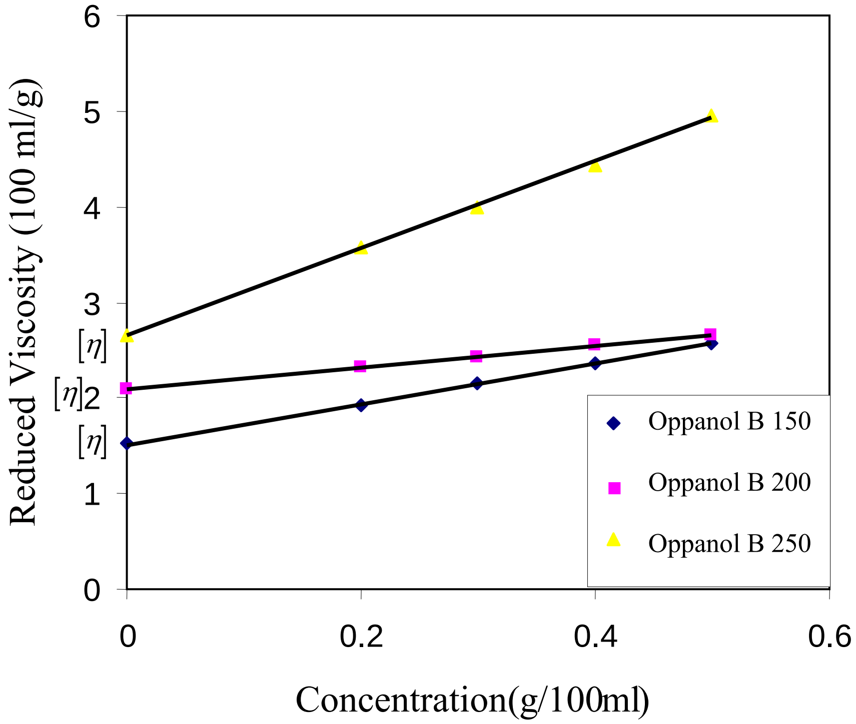


Figure 4-2 Reduced Viscosity Versus Concentration for Different Oppanol B in Crude Oil at Temperature 100°C.

Figures 4-1, and 4-2 show that the polyisobutylene (PIB) behaves as neutral polymers in crude oil. Neutral polymers have the property that reduced viscosity increase with increasing of polymer concentration, because the structure of PIB may not contains a carboxyl group (49). When the polymer behaves as polyelectrolyte, the reduced viscosity increases with decreasing polymer concentration, this usually observed in aqueous solution, occurs because the carboxyl group on the polymer chain can ionize in the polar solvent and the effective electrostatic repulsion which makes this polymer chain highly extended (72).

By using equation (2.3), $\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c$ and reduced viscosity equal to $\frac{\eta_{sp}}{c}$, from figures (4-1 and 4-2) the relation of reduced viscosity against concentration, usually gives a straight line, the slope of this line is equal to $k'[\eta]^2$ and intercept equals to $[\eta]$, so that Huggin's constant K' can be estimated with $[\eta]$ is known (17, 26), as shown in Tables 4-3, and 4-4

Table 4-3 Intrinsic Viscosity of Crude Oil with Different Oppanol B at Temperature (40 and 100°C).

Temperature (^{o}C)	Intrinsic Viscosity(ml/g)		
	Oppanol B 150	Oppanol B 200	Oppanol B 250
40	178	218	290
100	152	209	265

Table 4-4 Huggins Constant of Crude Oil with Different Oppanol B at Temperature (40 and 100°C).

Temperature (^{o}C)	Huggins constant(K')		
	Oppanol B 150	Oppanol B 200	Oppanol B 250
40	0.224	0.22	0.24
100	0.9	0.26	0.42

Figures 4-1, and 4-2 show that the hydrodynamic volume $[\eta]$ of PIB in crude oil decreases with increasing the temperature. The interaction of PIB in crude oil becomes an unfavorable with increasing temperature due to decreasing the solvent power of crude oil, which suggests that PIB coil tend to shrink at higher temperatures, this result agreed with previous literature for PIB in cyclohexane and carbon tetrachloride (53).

By using equation 2.1, $[\eta] = KM^{a}$ a plot of the $\log[\eta]$ versus log M for PIB in crude oil at 40°C usually gives a straight line, the slope of this line is the "a" value and the intercept equals to the log K (17), the results were shown in Figure 4-3 and Table A-7, Appendix A. These results have been compared for PIB in crude oil with other solvents in previous literatures (20, 21), as shown in Table 4-5.

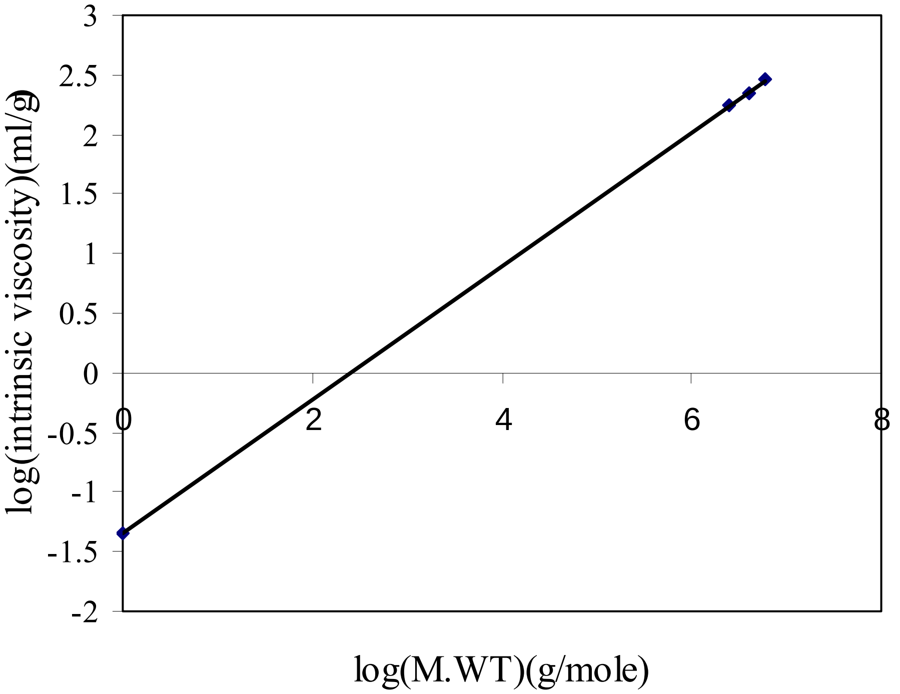


Figure 4-3 log (molecular weight) verse log (intrinsic viscosity) for Different Oppanol B in Crude Oil at Temperature 40°C.

Table 4-5 Mark-Houwink Parameters for Polyisobutylene in Crude Oil and Compared with Previous Literature (20, 21)

Polymer	Solvent	Temperature/°C	K (cm^3/g)	a
Polyisobutylene	Benzene	30	0.061	0.56
	Toluene	30	0.02	0.67
	Cyclohexane	30	0.0276	0.69
	Carbon tetrachloride	30	0.029	0.68
	Crude oil	40	0.0442	0.558

Mark-Houwink parameters (K and a) are constants for PIB in crude oil at temperature 40^{o}C as shown in Table 4-5, then the increasing of molecular weight causes an increasing in the intrinsic viscosity as shown in Table 4-3 according to Mark –Houwink parameter.

4.2.2 Intrinsic Viscosity of Olefin Copolymer in Crude Oil

Olefin copolymer is manufacturing by different companies with unknown structure, to produce the best additives used for different purposes (such as, increasing viscosity index, or reducing drag reduction). Olefin copolymer (OCP) with three different Viscoplex-4-677, Viscoplex 215496, and Lubrizol R 7077 dissolved in crude oil by magnetic stirrer. The time of dissolved 2grams per 100 ml (w/v) for three different OCP takes 2hr, and then diluted to different concentrations for 30 seconds.

- OCP (Viscoplex-4-677) was dissolved in crude oil; the effect of changing the concentration on reduced viscosity is represented graphically for two temperatures (40 and 100°C) as shown in Figures 4-4, and 4-5 respectively, and the results shown in Tables 4-6 and A-8, A-9 in Appendix A.
- For OCP (Viscoplex (215496)), the results shown in Figures 4-6, and 4-7 respectively, and Tables 4-7 and A-10, A-11 in Appendix A.
- For OCP (Lubrizol R7077), the results shown in Figures 4-8, and 4-9 respectively, and Tables 4-8 and A-12, A-13 in Appendix A.

Table 4-6 Reduced Viscosity of Crude Oil with OCP (Viscoplex-4-677)

Conc.(w/v)	$\eta_{red} = \eta_{sp}$/conc.(100ml/g)	
	Temperature 40 °C	Temperature 100 °C
2g/100ml	0.62	0.52
1.6g/100ml	0.61	0.49
1g/100ml	0.6	0.46
0.6g/100ml	0.57	0.416

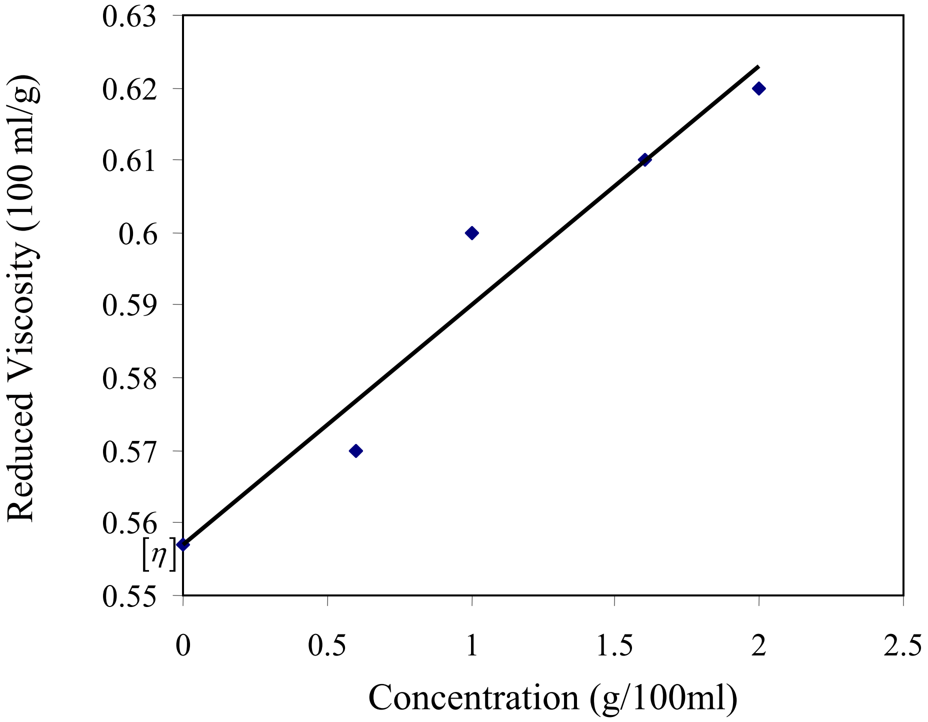


Figure 4-4 Reduced Viscosity Versus Concentration for OCP (Viscoplex-4-677) in Crude Oil at Temperature 40°C.

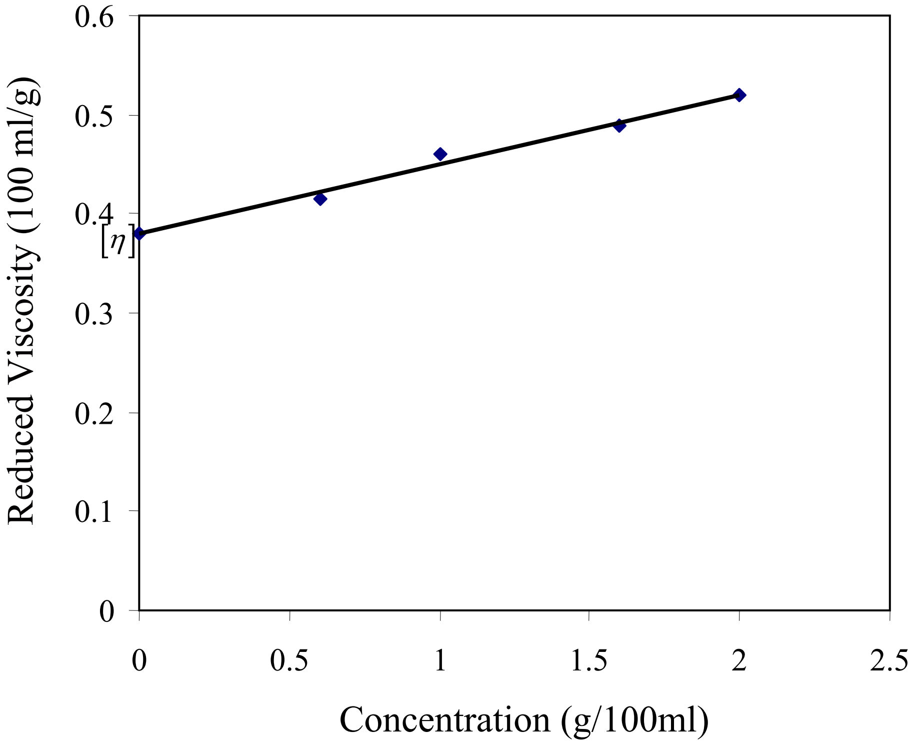


Figure 4-5 Reduced Viscosity Versus Concentration for OCP (Viscoplex-4-677) in Crude Oil at Temperature 100°C.

Table 4-7 Reduced viscosity of Crude Oil with OCP (Viscoplex-215496)

Conc.(w/v)	$\eta_{red} = \eta_{sp}/conc.(100ml/g)$	
	Temperature 40 ^{o}C	Temperature 100 ^{o}C
2g/100ml	0.25	0.125
1.8g/100ml	0.28	0.2
1.6g/100ml	0.31	0.25
1.4g/100ml	0.34	0.285
1g/100ml	0.41	0.4
0.5g/100ml	0.47	0.5

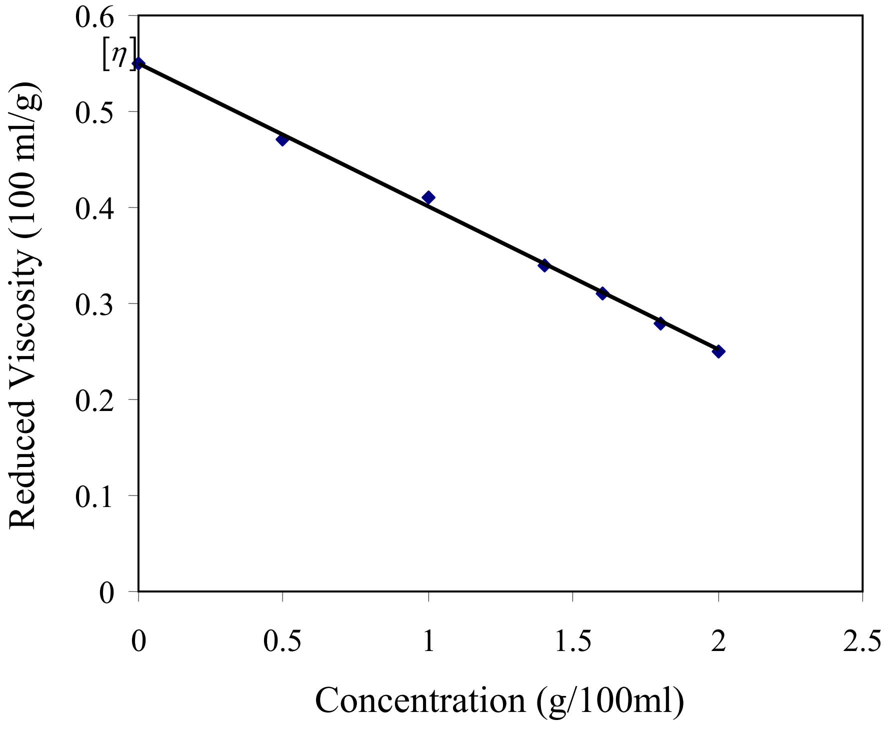


Figure 4-6 Reduced Viscosity Versus Concentration for OCP (Viscoplex-215496) in Crude Oil at Temperature 40°C.

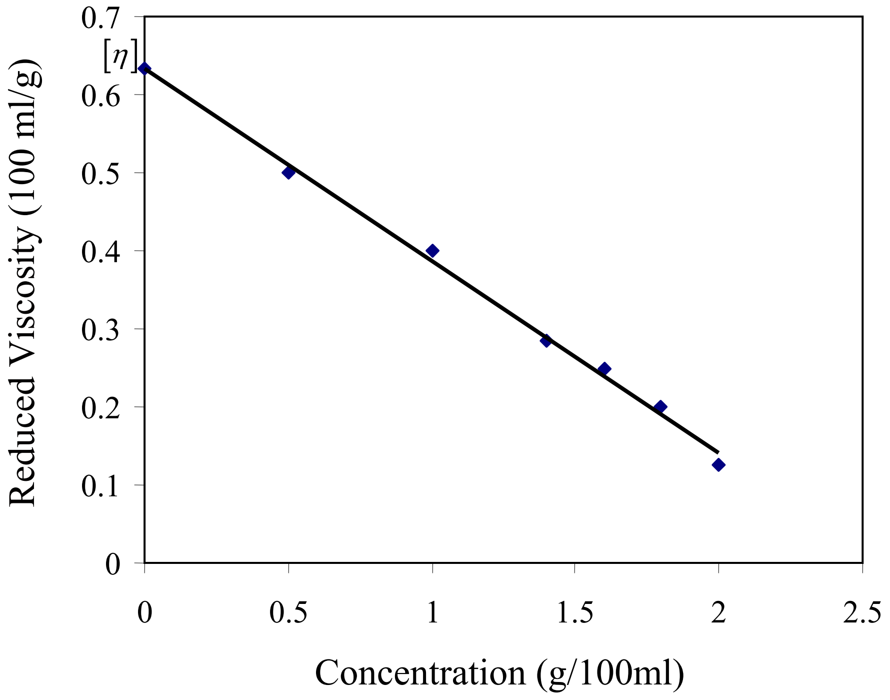


Figure 4-7 Reduced Viscosity Versus concentration for OCP (Viscoplex-215496) in Crude Oil at Temperature 100° C.

Table 4-8 Reduced Viscosity of Crude Oil with OCP (Lubrizol R 7077)

Conc.(w/v)	$\eta_{red} = \eta_{sp}$/conc.(100ml/g)	
	Temperature 40 °C	Temperature 100 °C
2g/100ml	0.22	0.33
1.8g/100ml	0.25	0.34
1.6g/100ml	0.27	0.35
1.2g/100ml	0.37	0.37
1g/100ml	0.42	0.38
0.8g/100ml	0.48	0.4

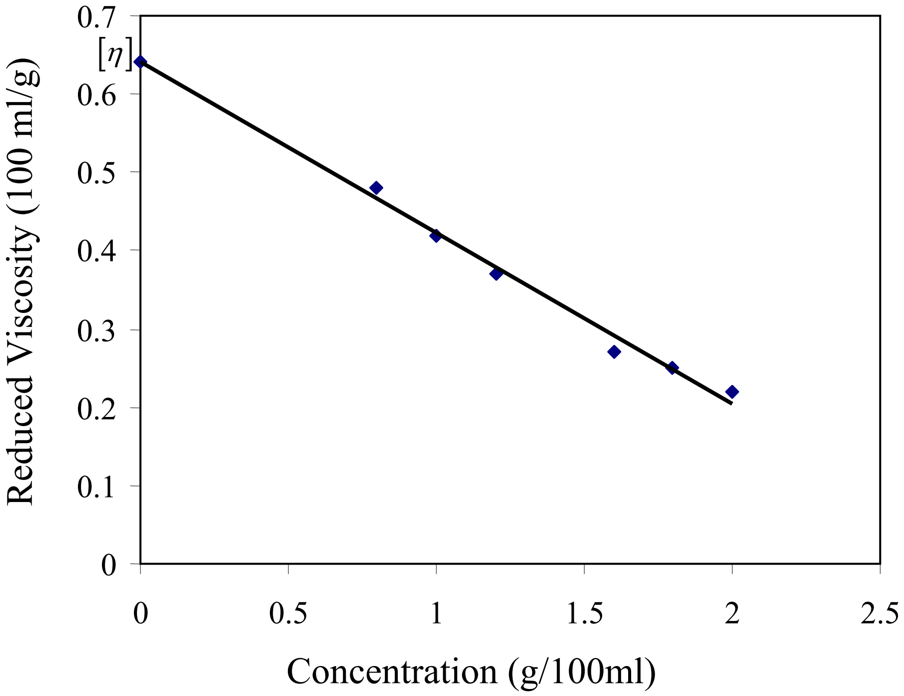


Figure 4-8 Reduced Viscosity Versus Concentration for OCP (Lubrizol R7077) in Crude Oil at Temperature 40° C.

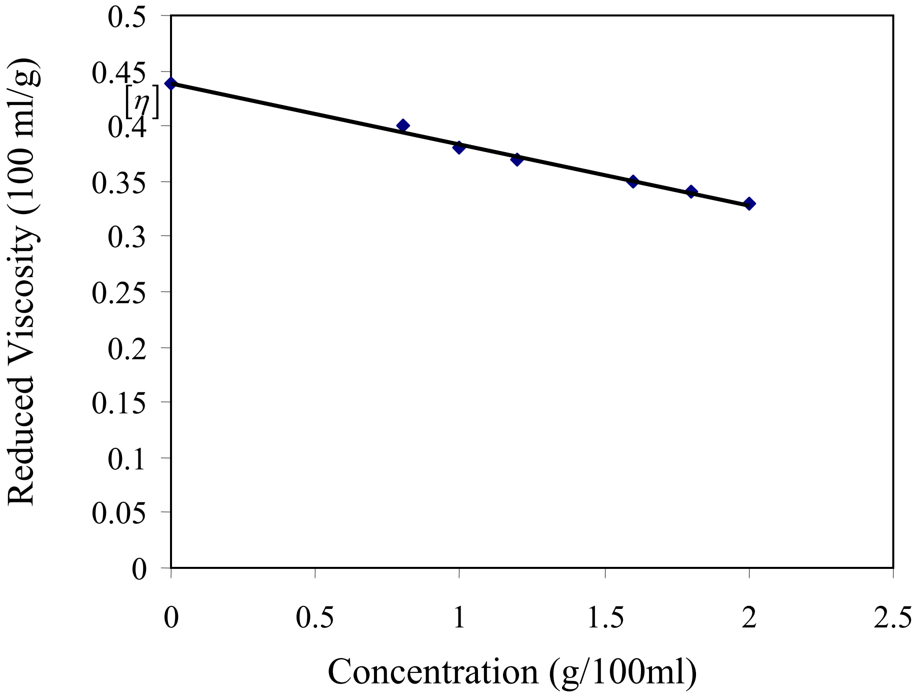


Figure 4-9 Reduced Viscosity Versus Concentration for OCP (Lubrizol R7077) in Crude Oil at Temperature 100° C.

Figures 4-4 to 4-9 show two types of olefin copolymers (OCP), the first type is (Viscoplex-4-677), which behaves as neutral polymers, neutral polymers have the property that reduced viscosity increase with increasing concentration, the second types are (Viscoplex-215496 and Lubrizol R7077), which behave as polyelectrolyte, where the reduced viscosity increases with decreasing concentration. The behavior of OCP as neutral and polyelectrolyte is not known, because the structure of OCP is unknown.

By using equation 2.3, $\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c$ and reduced viscosity equals to $\frac{\eta_{sp}}{c}$, from figures (4-4 to 4-9) the relation of reduced viscosity against concentration, usually gives a straight line, the slope of line equals to $k'[\eta]^2$ and its intercept equals to $[\eta]$, then Huggin's constant K' can be estimated with known $[\eta]$ (17, 26), as shown in Tables 4-9, to 4-10

Table 4-9 Intrinsic Viscosity of Crude Oil with Different OCP at Temperature (40 and 100°C).

Temperature (^oC)	Intrinsic Viscosity(ml/g)		
	Viscoplex-4-677	Viscoplex215496	Lubrizol R7077
40	55.7	55	64
100	37.9	63.3	43.9

Table 4-10 Huggins constant of Crude Oil with Different OCP at Temperature (40 and 100°C).

Temperature (^oC)	Huggins constant (K')		
	Viscoplex-4-677	Viscoplex215496	Lubrizol R7077
40	0.351	0.49	0.61
100	0.44	0.54	0.47

Figures (4-4, and 4-5) show that the OCP (Viscoplex-4-677) dissolved in crude oil behaves as polyisobutylene, show that the intrinsic viscosity decreases with increasing the temperature, so that, this behavior of (Viscoplex-4-677) can be used in crude oil as drag reduction agent like polyisobutylene.

4.3 Intrinsic Viscosity of Additives Added to Gas Oil

The relative, specific and reduced viscosities were measured using Ubbelohde capillary viscometer to estimate the intrinsic viscosity for polyisobutylene at different molecular weights at two temperatures (40 and 100 °C).

4.3.1 Intrinsic Viscosity of Polyisobutylene in Gas Oil

Polyisobutylene, Oppanol B type with three different molecular weights shown above, the dissolving of 1grams per 100 ml of gas oil (w/v), for Oppanol B 150 takes 15 hours, Oppanol B 200 takes19 hours, and Oppanol B 250 takes 30 hours and then diluted to different concentrations for 30 seconds.

- Oppanol B 150, B 200 and B 250 were dissolved in gas oil; and the effect of concentration on reduced viscosity is represented graphically for two temperatures (40 and 100°C) as shown in Figures 4-10, and 4-11 respectively, and the results shown in tables 4-11, 4-12, A-14, A-15 , A-16, A-17, A-18 and A-19 in Appendix A.

Table 4-11 Reduced Viscosity of Gas oil with Different Oppanol B at Temperature 40°C

Conc.(w/v)	$\eta_{red} = \eta_{sp}$/conc.(100ml/g)		
	B 150	B 200	B 250
0.5g/100ml	5.63	11	___
0.2g/100ml	4.3	6.9	11.8
0.1g/100ml	3.86	5.8	9.4
0.09g/100ml	3.4	5.24	9.1
0.07	___	___	7.73

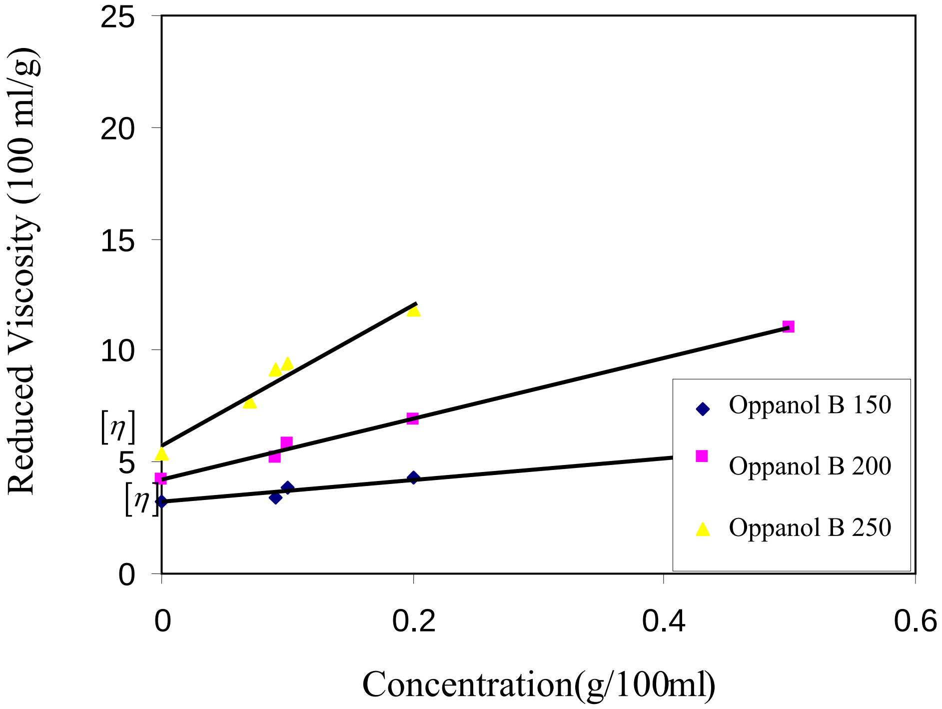


Figure 4-10 Reduced Viscosity Versus Concentration for Different Oppanol B in Gas Oil at Temperature 40°C.

Table 4-12 Reduced viscosity of Gas oil with Different Oppanol B at Temperature 100°C

Conc.(w/v)	$\eta_{red} = \eta_{sp}$/conc.(100ml/g)		
	B 150	B 200	B 250
0.5g/100ml	4.17	10.9	____
0.2g/100ml	3.1	5.88	10.29
0.1g/100ml	2.8	5	7.5
0.09g/100ml	2.5	4.24	7.18
0.07	____	____	5.46

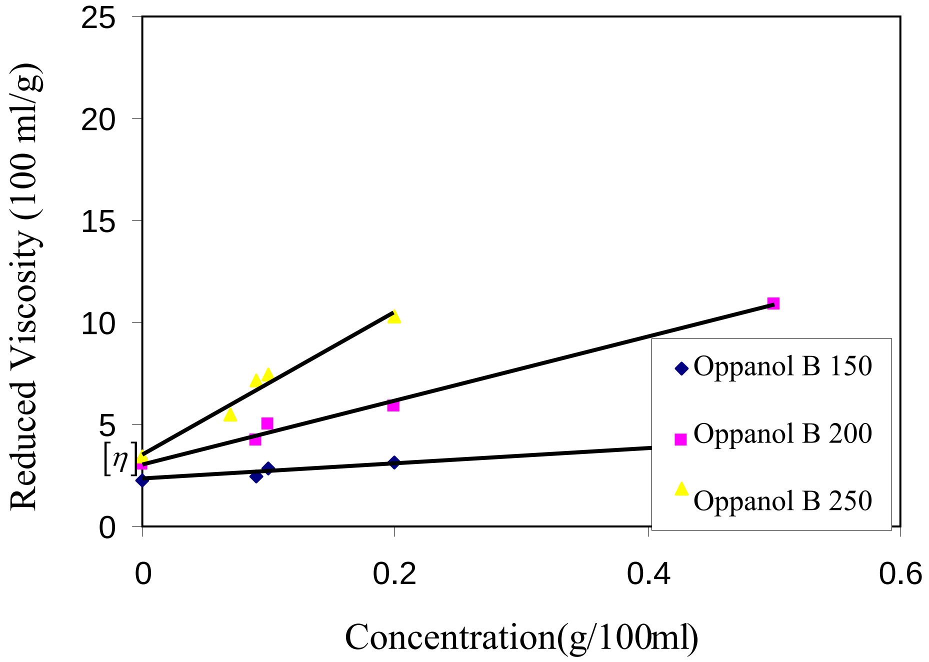


Figure 4-11 Reduced Viscosity Versus Concentration for Different Oppanol B in Gas Oil at Temperature 100°C.

Figures 4-10 and 4-11 show the behavior of polyisobutylene (PIB) in gas oil which has similar behavior of polyisobutylene in crude oil, (as neutral polymer), where the reduced viscosity increases with increasing the polymer concentration, because the structure of PIB dose not contain carboxylic group to behave as polyelectrolyte.

By using equation 2.3, $\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c$ and reduced viscosity equals to $\frac{\eta_{sp}}{c}$, figures (4-10 and 4-11) show the relation of reduced viscosity against concentration, the intrinsic viscosities and Huggins constants illustrated in Tables 4-13, and 4-14 respectively.

Table 4-13 Intrinsic Viscosity of Gas oil with different Oppanol B at Temperature (40 and 100°C).

Temperature (°C)	Intrinsic Viscosity(ml/g)		
	Oppanol B 150	Oppanol B 200	Oppanol B 250
40	320	421	541
100	230	303	340

Temperature (°C)	Huggins constant(K')

	Oppanol B 150	Oppanol B 200	Oppanol B 250
40	0.34	0.8	0.9
100	0.94	1.80	4.3

Table 4-14 Huggins constant of Gas oil with different Oppanol B at temperature (40 and 100°C)

Figures 4-10 and 4-11 show that the hydrodynamic volume $[\eta]$of PIB in gas oil decreases with increasing the temperature, which is similar to polyisobutylene in crude oil, the PIB in gas oil interaction becomes to be unfavorable when increasing temperature due to the decreasing of solvent power of gas oil, which suggests that PIB coil tend to shrink at higher temperatures, this result agreed with previous literature (31, 53, 61).

By using equation 2.1, $[\eta] = KM^{a}$, a plot of the log $[\eta]$ versus log M for PIB in gas oil at a temperature of 40°C usually gives a straight line, the slope of this line is the "a" value and the intercept equals to the log K(17), the result show in Figure 4-12 and Table A-20, Appendix A. The results of this work compared for PIB in crude and gas oil with other solvent in previous literature (20, 21), as shown in Table 4-15

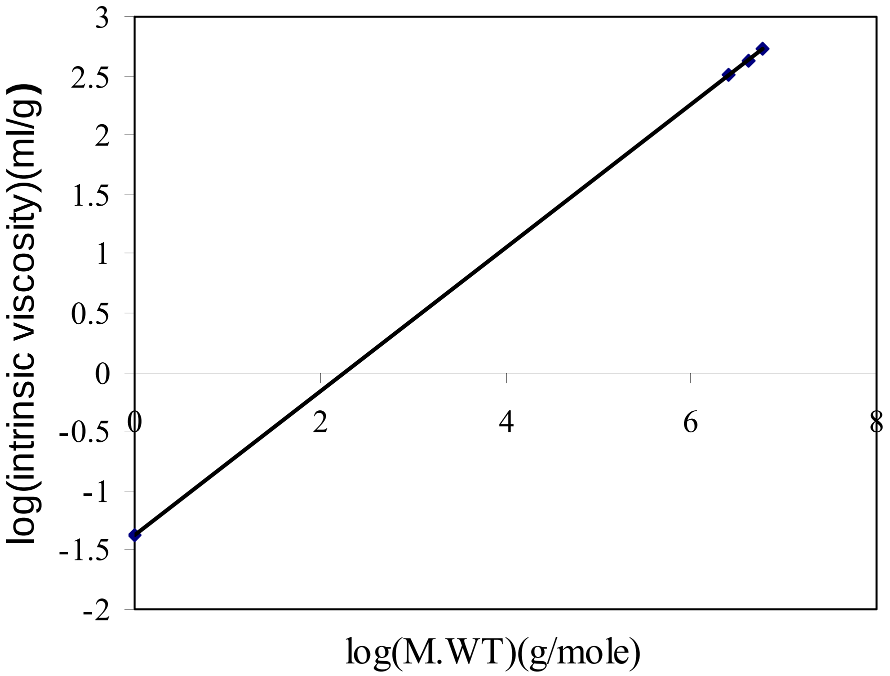


Figure 4-12 Log (molecular weight) verse log (intrinsic viscosity) for different Oppanol B in Gas oil at Temperature 40°C.

Table 4-15 Mark-Houwink parameters for Polyisobutylene in Crude and Gas Oil and Compared with Other Solvent in Previous Literature (20, 21)

Polymer	Solvent	Temperature/^oC	k (cm^3/g)	a
Polyisobutylene	Benzene	30	0.061	0.56
	Toluene	30	0.02	0.67
	Cyclohexane	30	0.0276	0.69
	Carbon tetrachloride	30	0.029	0.68
	Crude oil	40	0.0442	0.558
	Gas oil	40	0.0415	0.6

Table 4-13 shows that the intrinsic viscosity of PIB in gas oil is higher than that in crude oil as shown in Table 4-3 at the same temperature, this is because the difference in Mark-Houwink parameter (K and a) in gas and crude oil as shown in Table 4-15.

4.4 Intrinsic Viscosity of Additives Added in Water

The relative, specific and reduced viscosities were measured by using Ubbelohde capillary viscometer to estimate the intrinsic viscosity for Xanthan Gum and polyacrylamid at temperatures 40°C.

4.4.1 Intrinsic Viscosity of Xanthan Gum in Water

Xanthan Gum (XG) of molecular weight $3.7*10^6$ dissolved in water by magnetic mixer. The time of dissolved 2grams of (XG) per 100 ml of water (w/v), takes 6 days and then diluted to different concentrations for 30 seconds.

- Xanthan Gum was dissolved in water; the effect of changing the concentration on reduction viscosity is represented graphically for temperatures 40°C as shown in Figure 4-13, and the results shown in Tables 4-16 and A-21 in Appendix A.

Table 4-16 Reduced viscosity of water with XG

Conc.(w/v)	$\eta_{red} = \eta_{sp}$/conc.(100ml/g)
	Temperature 40 ^oC
2g/100ml	0.11
1.8g/100ml	0.15
1.6g/100ml	0.195
1.4g/100ml	0.28
1.2g/100ml	0.32
1g/100ml	0.37

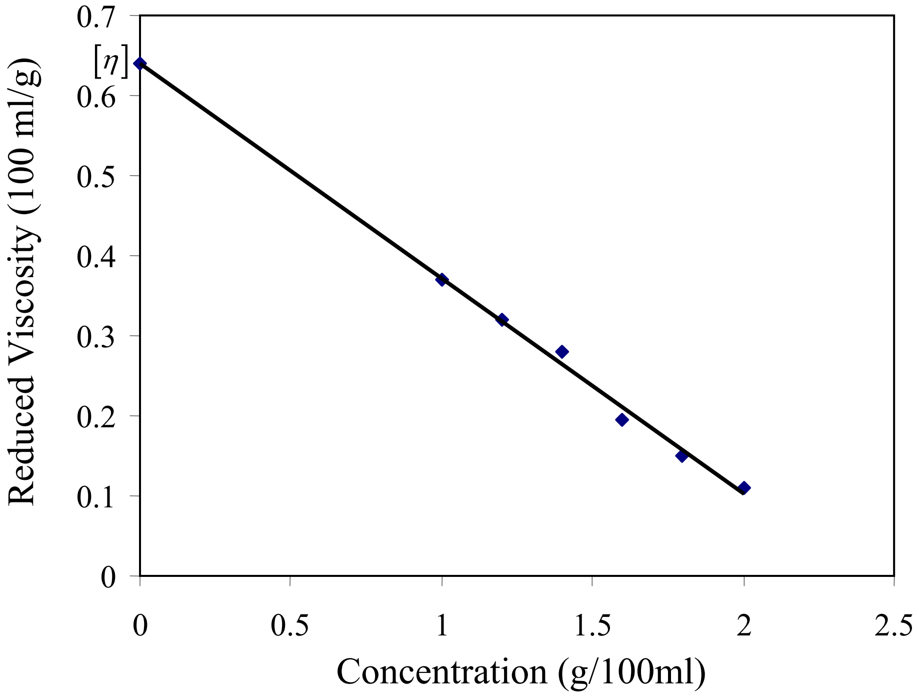


Figure 4-13 Reduced Viscosity Versus Concentration for XG in Water at Temperature 40°C.

4.4.2 Intrinsic Viscosity of Polyacrylamid in Water

polyacrylamid (PAM) of high molecular weight dissolved in water by magnetic mixer. The time of dissolved 0.026 grams per 100 ml (w/v), of (PAM) takes 3 days and then diluted to different concentration for 30 seconds.

- polyacrylamide was dissolved in water, the effect of changing concentration on the reduction viscosity is represented graphically for the temperature of 40°C as in Figure 4-14 , and the results shown in Tables 4-17 and A-22 in Appendix A.

Table 4-17 Reduced viscosity of water with PAM

Conc.(w/v)	$\eta_{red} = \eta_{sp}$/conc.(100ml/g)
	Temperature 40 °C
0.026g/100ml	57.3
0.02g/100ml	50
0.018g/100ml	49.2
0.013g/100ml	48
0.09g/100ml	41.3

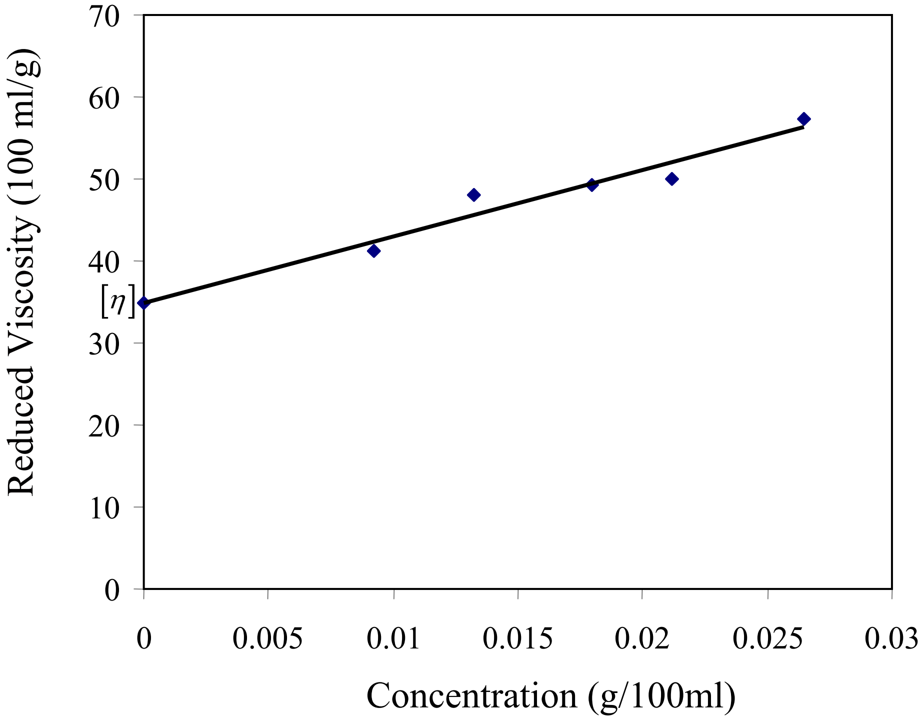
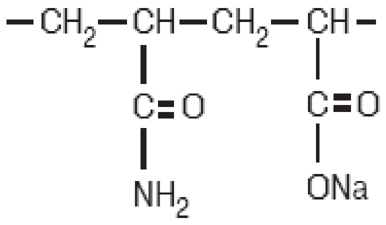


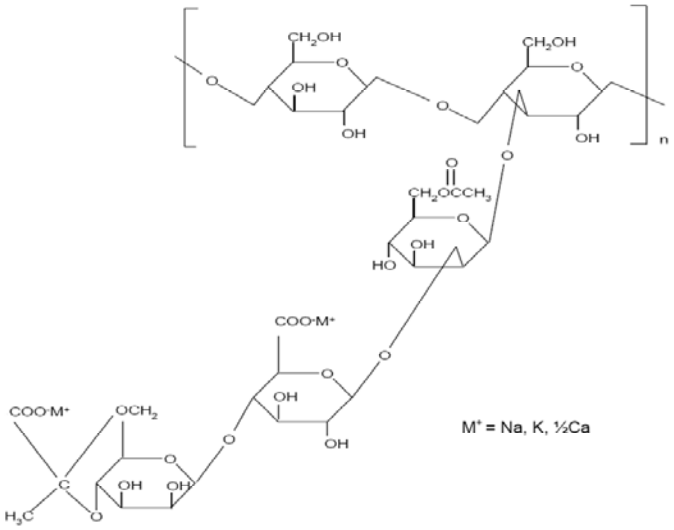
Figure 4-14 Reduced Viscosity Versus Concentration for PAM in Water at Temperature 40°C.

Figures 4-13, and 4-14 show the concentration effect on the reduced viscosity for polymers dissolved in water, where the polyacrylamide(PAM) behaves as neutral polymer as reduced viscosity increases with increasing the polymer concentration, although water is polar solvent but the polymer behaves as polyelectrolyte must contain a carboxyl group, such as polyacrylic acid dissolved in water as shown in chapter two(66), and polyelectrolyte depends also on the solution ph, counterion concentration, or ionic strength(69), partially hydrolyzed polyacrylamide by copolymerization of acrylamide and sodium acrylate can behave as polyelectrolyte as shown in previous literature(72).The chemical structure of partially hydrolyzed polyacrylamide is as shown below(72):



$$-CH_2-\underset{\substack{|\\ C=O\\ |\\ NH_2}}{CH}-CH_2-\underset{\substack{|\\ C=O\\ |\\ ONa}}{CH}-$$

Xanthan gum (XG) behaves as polyelectrolyte as reduced viscosity increases with decreasing the polymer concentration because it may be contains a carboxyl group as shown below (35)



And water is polar solvent, then the carboxyl group when dissolved in water will have negative charges, and the repulsion forces between ionized carboxyl groups which makes XG chain highly extended.

Xanthan Gum used as drag reduction agent as in the previous works (94, 95, and 96), this polymer behaves as polyelectrolyte and it is good as drag reduction agent because the polymer chain will be extended and also simulate the deportment of linear random-coiling macromolecules in solution, this indicates a possible relationship between the mechanisms of drag reduction produced by these additives (97).

By using equation 2.3, $\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c$ and reduced viscosity equals to $\frac{\eta_{sp}}{c}$, figures (4-13 and 4-14) show the relation of reduced viscosity against concentration, the intrinsic viscosities and Huggins constants illustrated in Table 4-20

Table 4-18 Intrinsic Viscosity and Huggin constant for xanthan gum and polyacrylamide at temperature 40°C

Temperature 40 (°C)	Xanthan gum	polyacrylamide
Intrinsic Viscosity(ml/g)	64	349
Huggins constant (K')	0.17	0.74

4.5 Flow Activation Energy of Crude Oil

Measurements for dynamic viscosities of crude oil in the range of temperatures of 30-70 °C using rotational viscometer were studied. The Arrhenius-Erying equation(2.17) was used, and the log μ was plotted versus 1/T at a given shear rate to get a straight line and the slope of the line was calculated, the flow activation energy of crude oil, E_0, was obtained by multiplying the slope of the line by (2.303*R), where R is the universal gas constant equals to 8.314J/ mole.K, the flow activation energy of crude oil is represented in Figure 4-15 and Table 4-19, this result agreed with previous literatures which measure the flow activation energy of this type and other different types of crude oil (88).

Table 4-19 Temperature Dependence of Crude Oils Dynamic viscosity

Temperature(k)	Crude oil
	dynamic viscosity(cp)
303.15	9.8
313.15	9
323.15	8.1
333.15	7.4

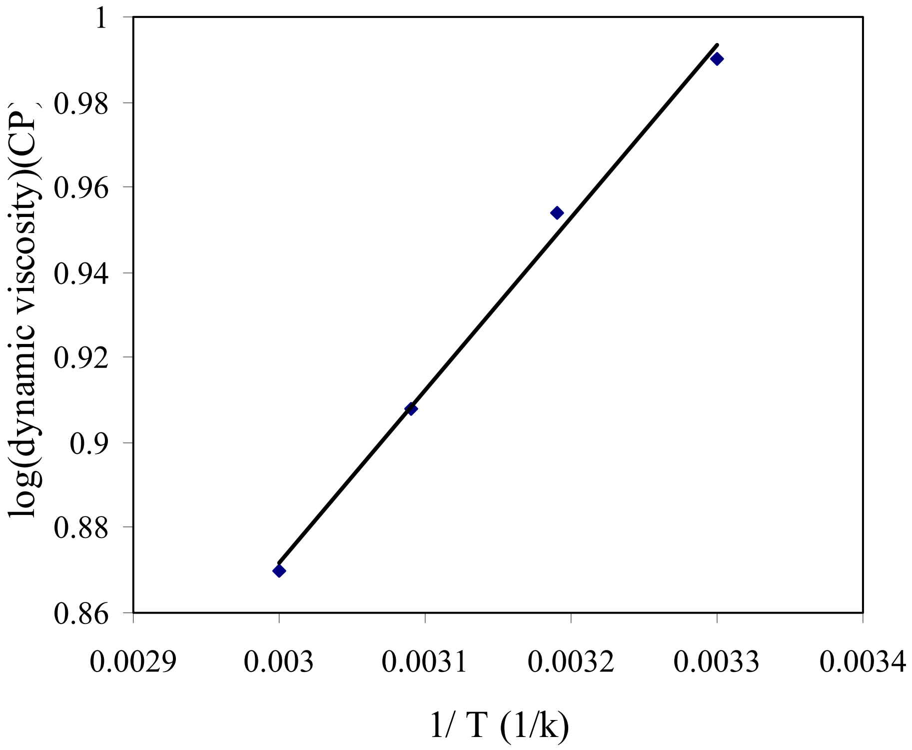


Figure 4-15 Log (dynamic viscosity) versus **(**1/ temperature) for Crude Oil at Shear Rate 100 rpm

4.5.1 Flow Activation Energy of Polyisobutylene Added to Crude Oil

Measurements of dynamic viscosities for polyisobutylene (Oppanol B type) in crude oil were studied, with three different molecular weights, $2.5*10^6$ g/mole for Oppanol 150, $4.1*10^6$ for Oppanol 200 and $5.9*10^6$ for Oppanol 250, by using rotational viscometer in the range of temperatures of 30-70 °C. As in the previous section the Arrhenius-Erying equation (2.17) was used, and the log μ was plotted versus 1/T at a given shear rate to get a straight line and the slope of the line was calculated, the flow activation energy of oppanol B in crude oil, E, was obtained by multiplying the slope of the line by (2.303*R), where R is universal gas constant and equal to 8.314J/mole.K.

- The measurements of dynamic viscosities of Oppanol B 150 in crude oil at temperatures 30-70 °C, for different concentrations, were represented graphically in Figure 4-16, and the results shown in Table 4-20.
- The measurements of dynamic viscosities of Oppanol B 200 were represented graphically in Figure 4-18, and the results shown in Table 4-22.
- The measurements of dynamic viscosities of Oppanol B 250 were represented graphically in Figure 4-20, and the results shown in Table 4-24.

Table 4-20 Effect of Oppanol B 150 in Crude Oil at Different Concentration on Dynamic Viscosity.

Temperature (K)	Dynamic viscosity		
	Con.(0.5g/100ml)	Con.(1g/100ml)	Con.(2g/100ml)
303.15	130	330	386
313.15	117	307	374
323.15	105	268	368
333.15	99	263	355

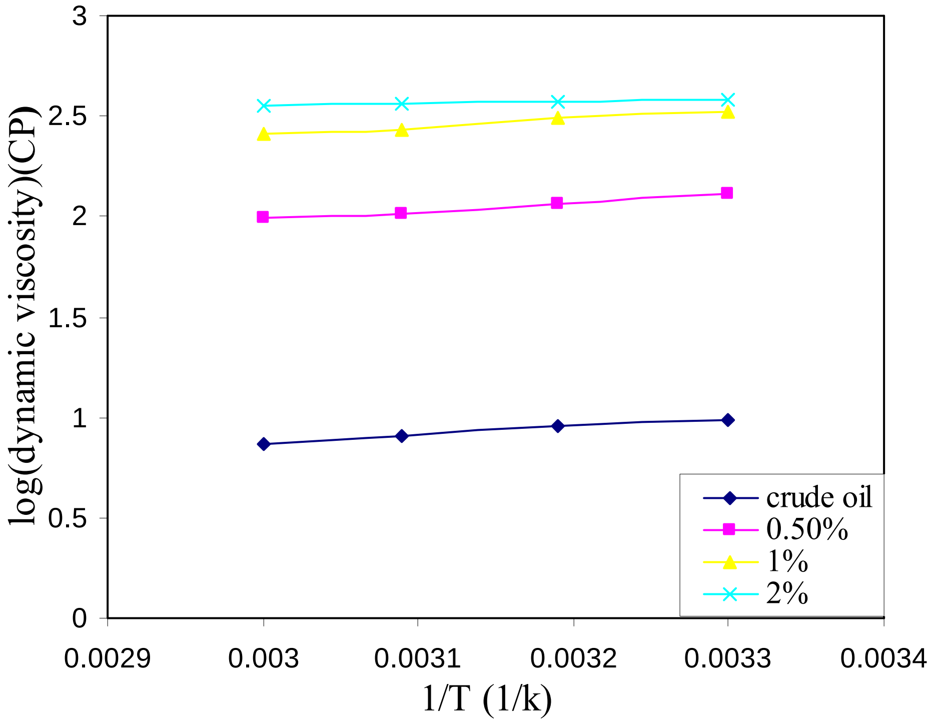


Figure 4-16 Log (dynamic viscosity) Versus **(**1/ temperature) for Oppanol B150 with Crude Oil at Different Concentration and Shear Rate 100 rpm.

Table 4-21 Relation of FAE with Concentration of Oppanol B 150 in Crude Oil

Concentration (g/ml)	Flow Activation Energy (KJ/mole)
Crude oil only	8.2
0.005	7.6
0.01	5
0.02	2.6

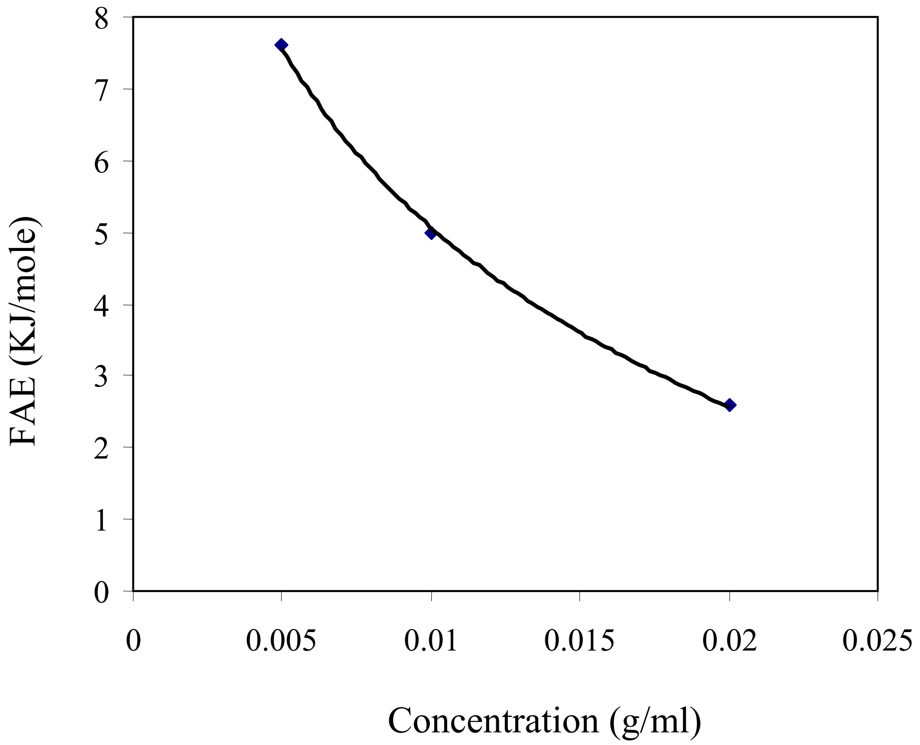


Figure 4-17 Flow Activation Energy Verse concentration for Oppanol B 150 in Crude Oil.

Table 4-22 Effect of Oppanol B 200 in Crude Oil at Different Concentration on Dynamic Viscosity.

Temperature (K)	Dynamic viscosity		
	Con.(0.5g/100ml)	Con.(1g/100ml)	Con.(2g/100ml)
303.15	103	256	290
313.15	97	239.8	281
323.15	86	223	272
333.15	77	213.7	263

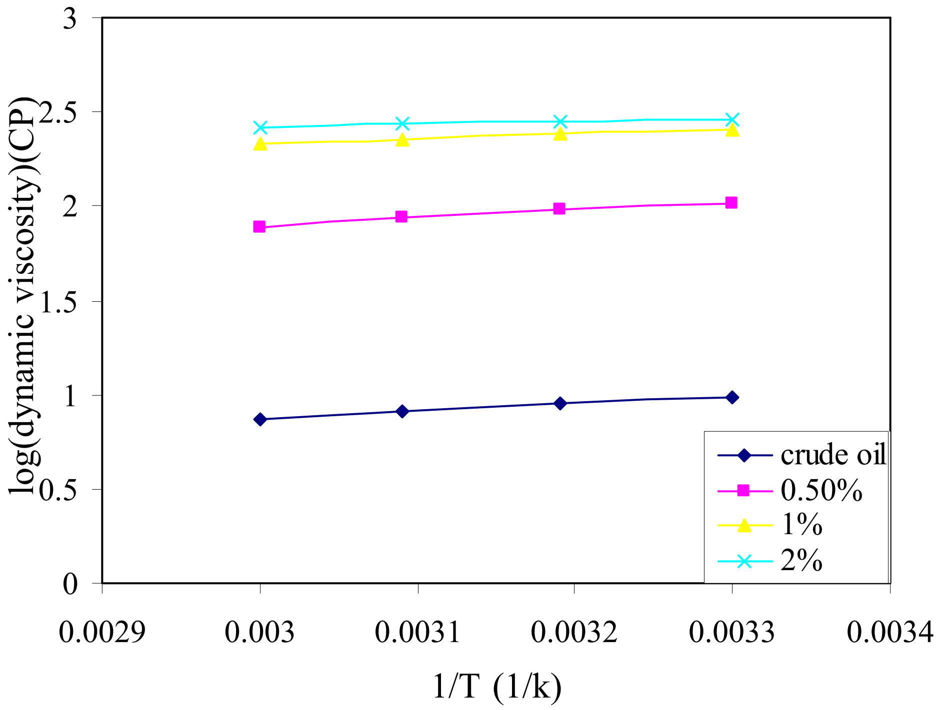


Figure 4-18 Log (dynamic viscosity) Versus (1/ temperature) for Oppanol B200 with Crude Oil at Different Concentration and Shear Rate 100 rpm.

Table 4-23 Relation of FAE with Concentration of Oppanol B 200 in Crude Oil

Concentration (g/ml)	Flow Activation Energy (KJ/mole)
Crude oil only	8.2
0.005	7.4
0.01	4.6
0.02	2.48

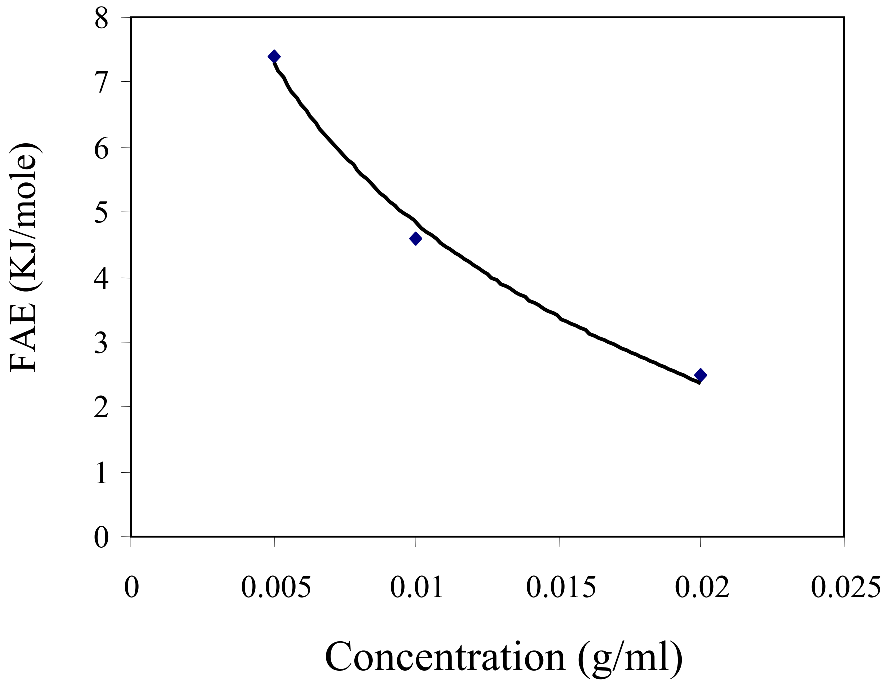


Figure 4-19 Flow Activation Energy Verse Concentration for Oppanol B 200 in Crude Oil.

Table 4-24 Effect of Oppanol B 250 in Crude Oil at Different Concentration on Dynamic Viscosity.

Temperature (K)	Dynamic viscosity		
	Con.(0.5g/100ml)	Con.(1g/100ml)	Con.(2g/100ml)
303.15	220	257	340
313.15	200	245	333
323.15	180	207	325
333.15	160	222	318

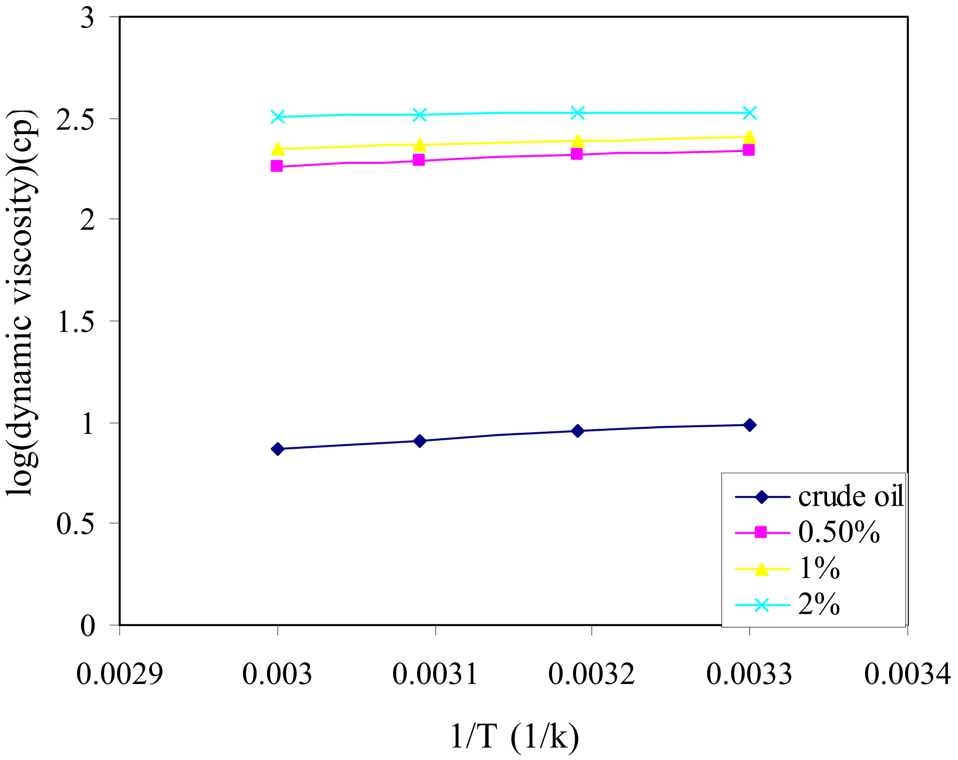


Figure 4-20 Log (dynamic viscosity) Versus **(**1/ temperature) for Oppanol B 250 with Crude Oil at Different Concentration and Shear Rate 100 rpm.

Table 4-25 Relation of FAE with Concentration of Oppanol B 250 in Crude Oil

Concentration (g/ml)	Flow Activation Energy (KJ/mole)
Crude oil only	8.2
0.005	5.2
0.01	3.6
0.02	1.75

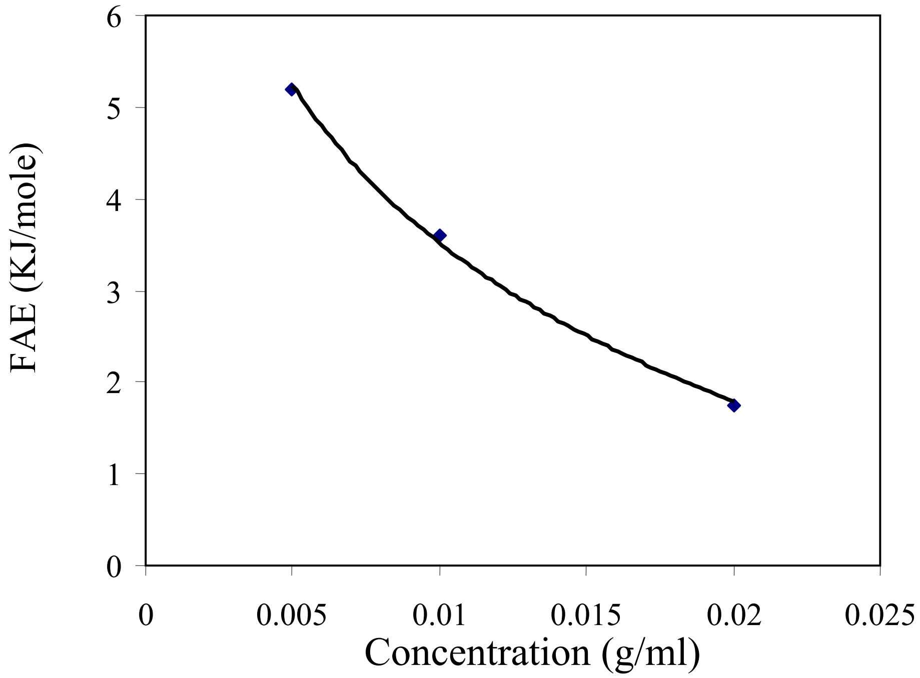


Figure 4-21 Flow Activation Energy Verse Concentration for Oppanol B 250 in Crude Oil.

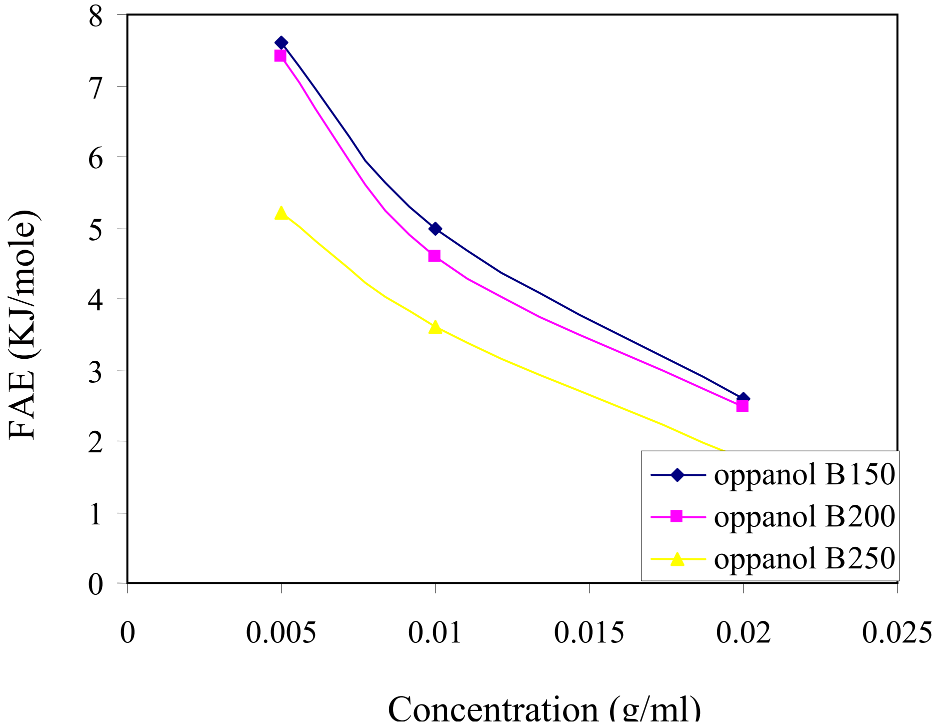


Figure 4-22 Flow Activation Energy Verse Concentration for Different Oppanol B in Crude Oil.

Table 4-26 Relation of FAE with Molecular weight of Oppanol B at Different Concentration in Crude Oil

Flow activation energy(FAE) (KJ/mole)			
Molecular weight	Con.(0.5g/100ml)	Con.(1g/100ml)	Con.(2g/100ml)
2.5*10^6	7.6	5	2.6
4.1*10^6	7.4	4.6	2.48
5.9*10^6	5.2	3.6	1.75

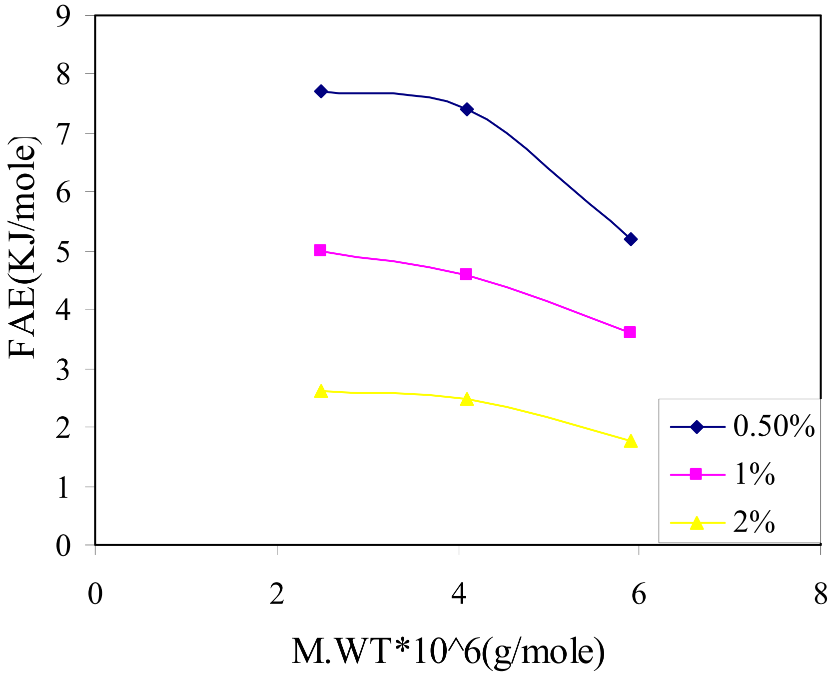


Figure 4-23 Flow Activation Energy Verse Molecular weight of Oppanol B at different concentration in crude oil.

Figures 4-17, 4-19, and 4-21 show that the flow activation energy decreases when increasing concentration of Oppanol B 150, 200, and 250 respectively in crude oil, these results greed with previous work (88) which uses commercial additives in crude oil

Figure 4-22 shows that the of flow activation energy decreases when increases the molecular weight of Oppanol B at different concentrations in crude oil.

Also, from Figure 4-23 it is clear that the flow activation energy decreases when increasing the concentration of Oppanol B at different molecular weights in crude oil.

4.6 Flow Activation Energy of Gas Oil

The measurements of dynamic viscosities of gas oil in the range of temperatures of 30-70 °C by using rotational viscometer were studied. The procedure for calculating of activation energy in gas oil is the same as that used for calculation of activation energy in crude oil and additives using Arrhenius-Erying equation, the flow activation energy of gas oil was represented in Figure 4-24 and Table 4-27.

Table 4-27 Temperature Dependence of Gas oils Dynamic viscosity

Temperature(k)	gas oil
	dynamic viscosity(cp)
303.15	15.4
313.15	13
323.15	10.2
333.15	9.77

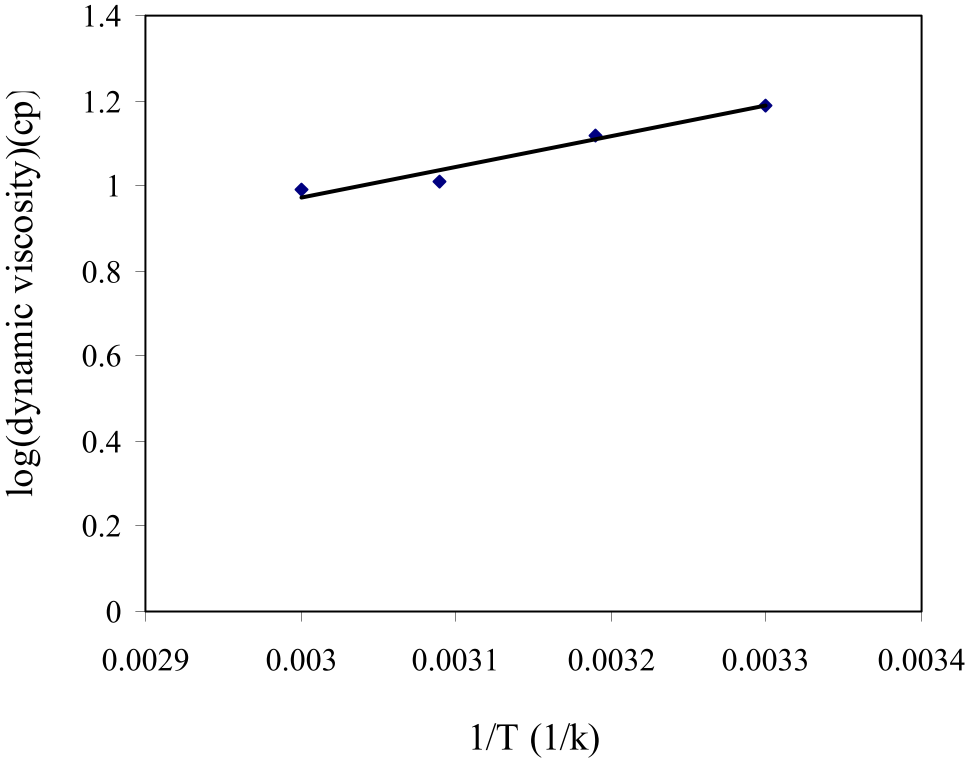


Figure 4-24 Log (dynamic viscosity) versus **(**1/ temperature) for Gas oil at Shear Rate 100 rpm

4.6.1 Flow Activation Energy of Polyisobutylene Added to Gas Oil

The measurements of dynamic viscosities for polyisobutylene Oppanol B type in gas oil were studied, with three different molecular weights, mentioned above, using rotational viscometer in the range of temperatures of 30-70 °C, the same procedure for calculation of activation energy in gas oil was used.

- The measurements of dynamic viscosities of Oppanol B 150 in gas oil at temperatures 30-70 °C, for different concentrations, were represented graphically in Figure 4-25, and the results shown in Table 4-28.
- The measurements of dynamic viscosities of Oppanol B 200 were represented graphically in Figure 4-27, and the results shown in Table 4-30.
- The measurements of dynamic viscosities of Oppanol B 250 were represented graphically in Figure 4-29, and the results shown in Table 4-32.

Table 4-28 Effect of Oppanol B 150 in Gas Oil at Different Concentration on Dynamic viscosity

Temperature (K)	Dynamic viscosity		
	Con.(0.5g/100ml)	Con.(1g/100ml)	Con.(2g/100ml)
303.15	19	236	357
313.15	17	209	338
323.15	13	183	328
333.15	12	163	308

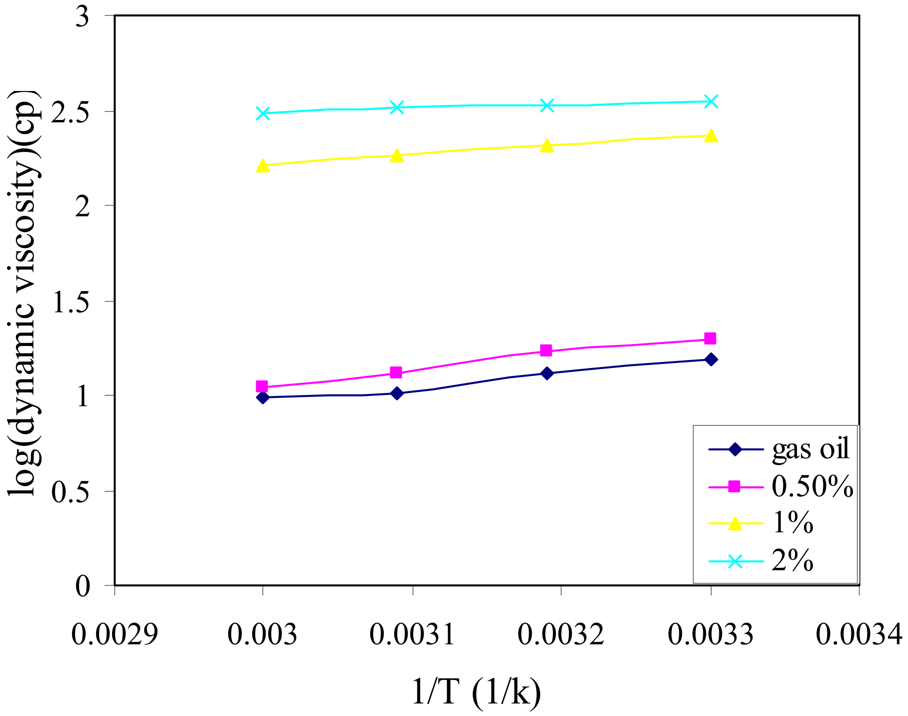


Figure 4-25 Log (dynamic viscosity) Versus (1/ temperature) for Oppanol B 150 with Gas oil at Different Concentration and Shear Rate 100 rpm.

Table 4-29 Relation of FAE with Concentration of Oppanol B 150 in Gas Oil

Concentration (g/ml)	Flow Activation Energy (KJ/mole)
gas oil only	17.8
0.005	15.3
0.01	10.4
0.02	3.82

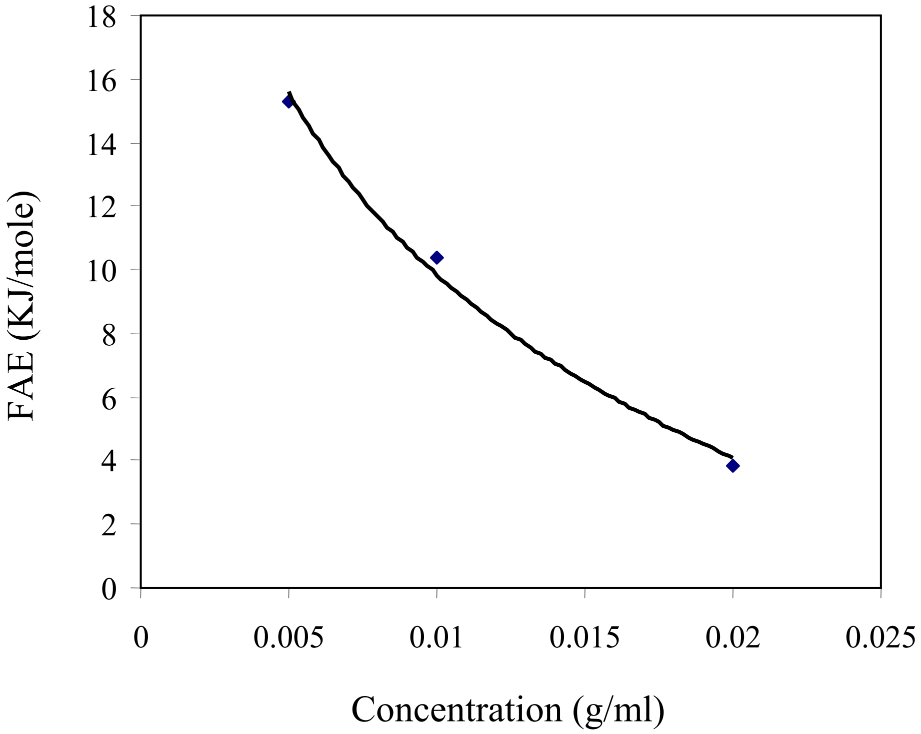


Figure 4-26 Flow Activation Energy Verse Concentration for Oppanol B 150 in Gas Oil

Table 4-30 Effect of Oppanol B 200 in Gas Oil at Different Concentration on Dynamic viscosity

Temperature (K)	Dynamic viscosity		
	Con.(0.5g/100ml)	Con.(1g/100ml)	Con.(2g/100ml)
303.15	51	80	546
313.15	41	68	531
323.15	33	62	510
333.15	29	57	492

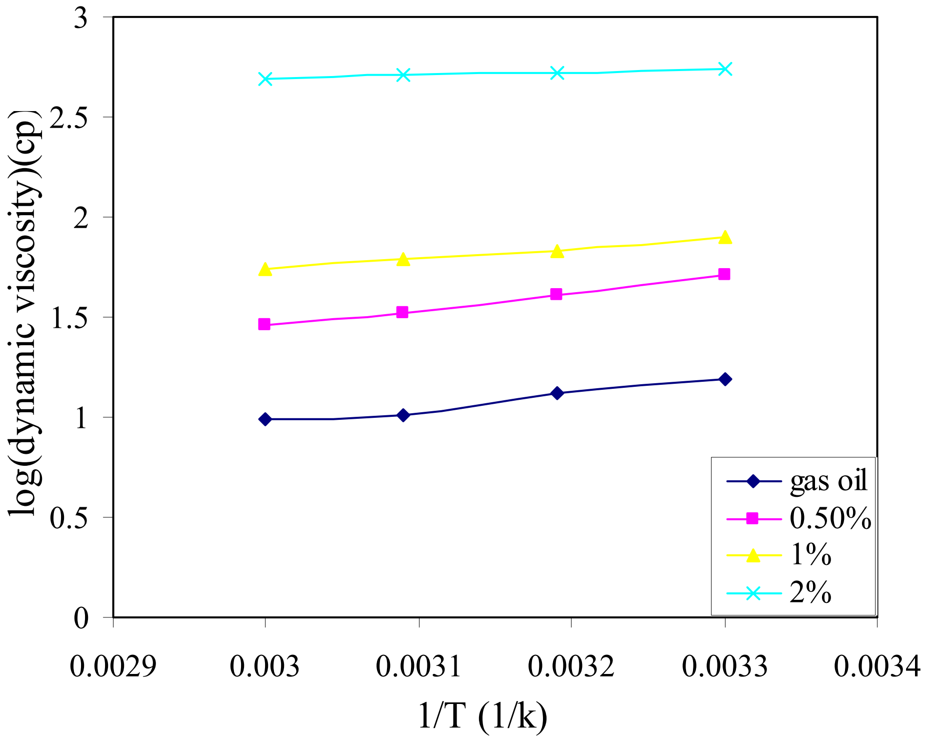


Figure 4-27 Log (dynamic viscosity) Versus (1/ temperature) for Oppanol B 200 with Gas Oil at Different Concentration and Shear Rate 100 rpm.

Table 4-31 Relation of FAE with Concentration of Oppanol B 200 in Gas Oil

Concentration (g/ml)	Flow Activation Energy (KJ/mole)
gas oil only	17.8
0.005	11.4
0.01	9.7
0.02	3.2

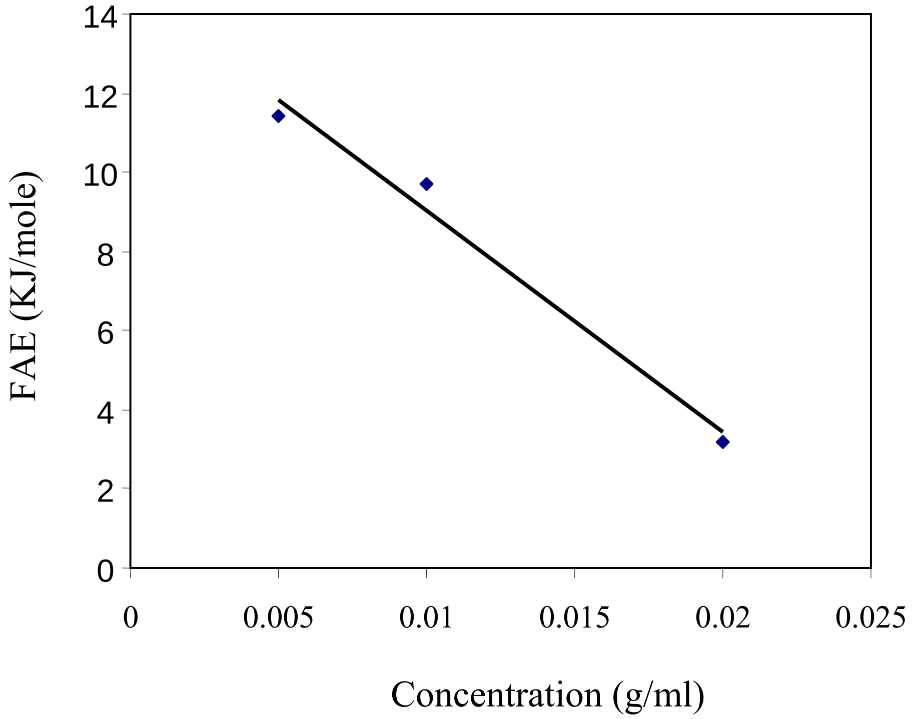


Figure 4-28 Flow Activation Energy verse Concentration for Oppanol B 200 in Gas Oil

Table 4-32 Effect of Oppanol B 250 in Gas Oil at Different Concentration on Dynamic viscosity.

Temperature (K)	Dynamic viscosity		
	Con.(0.5g/100ml)	Con.(1g/100ml)	Con.(2g/100ml)
303.15	187	276	340
313.15	166	264	329
323.15	148	260	316
333.15	130	247	309

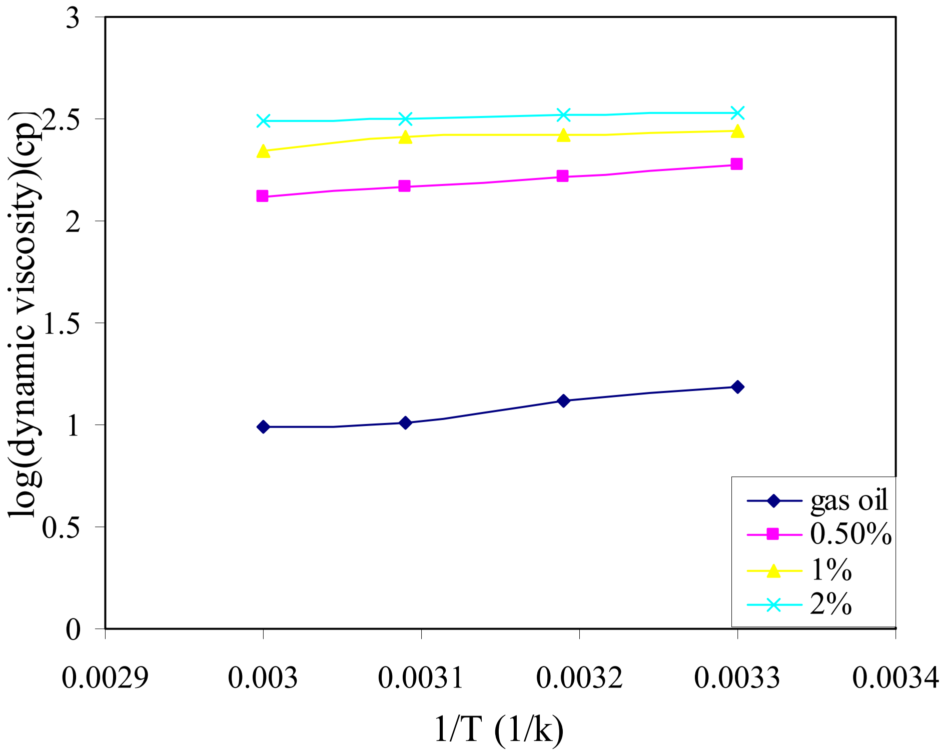


Figure 4-29 Log (dynamic viscosity) Versus **(**1/ temperature) for Oppanol B 250 with Gas oil at Different Concentration and Shear Rate 100 rpm.

Table 4-33 Relation of FAE with Concentration of Oppanol B 250 in Gas Oil

Concentration (g/ml)	Flow Activation Energy (KJ/mole)
gas oil only	17.8
0.005	10.4
0.01	6.03
0.02	2.8

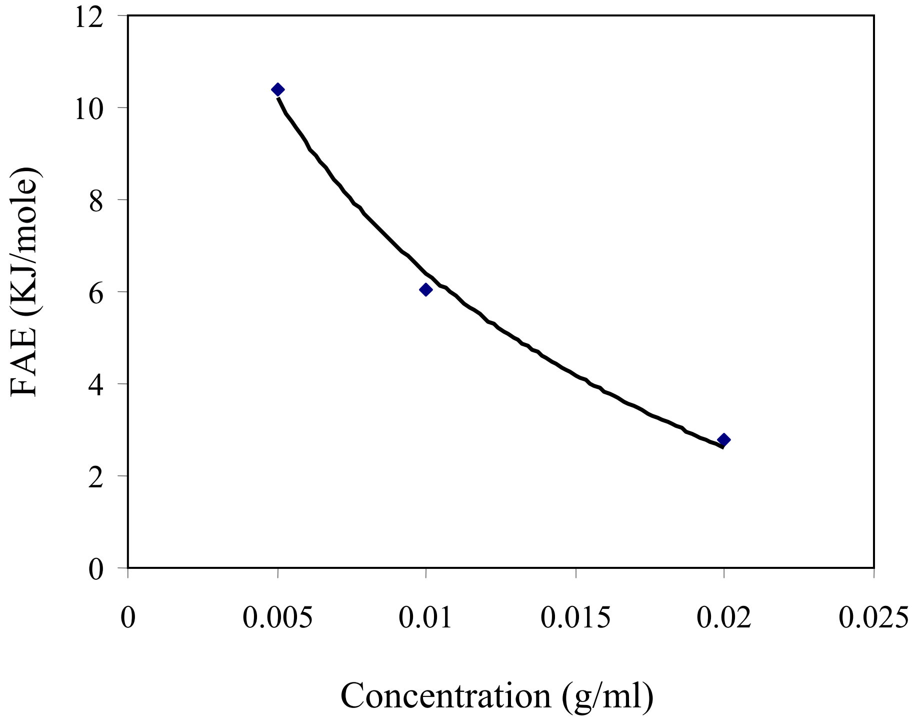


Figure 4-30 Flow Activation Energy Verse Concentration for Oppanol B 250 in Gas Oil

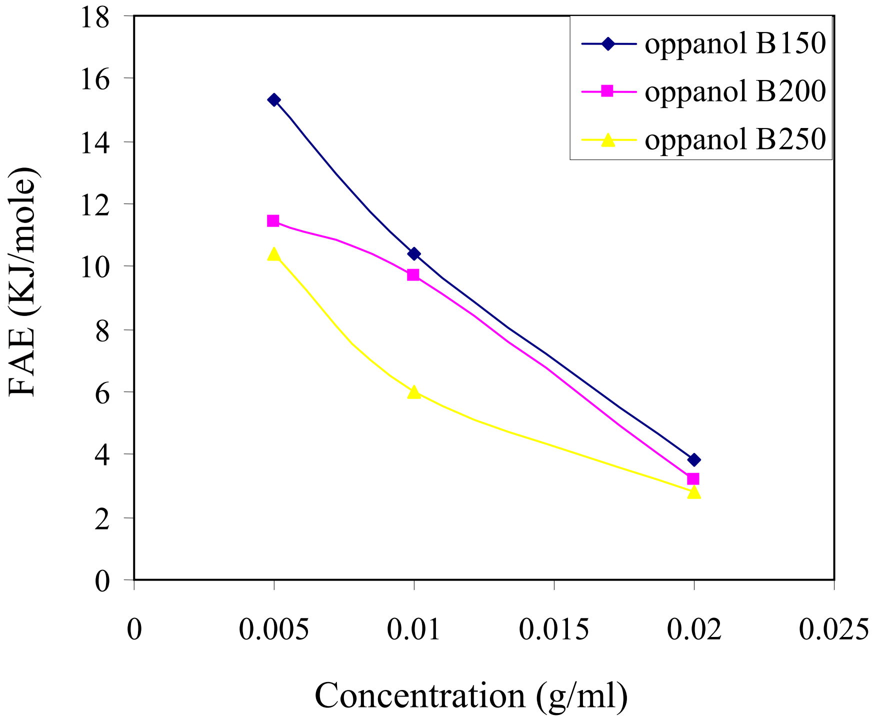


Figure 4-31 Flow Activation Energy Verse Concentration for Different Oppanol B in Gas Oil

Table 4-34 Relation of FAE with Molecular Weight of Oppanol B at Different Concentration in Gas Oil

Flow activation energy(FAE) (KJ/mole)			
Molecular weight	Con.(0.5g/100ml)	Con.(1g/100ml)	Con.(2g/100ml)
2.5*10^6	15.3	10.4	3.82
4.1*10^6	11.4	9.7	3.2
5.9*10^6	10.4	6.03	2.8

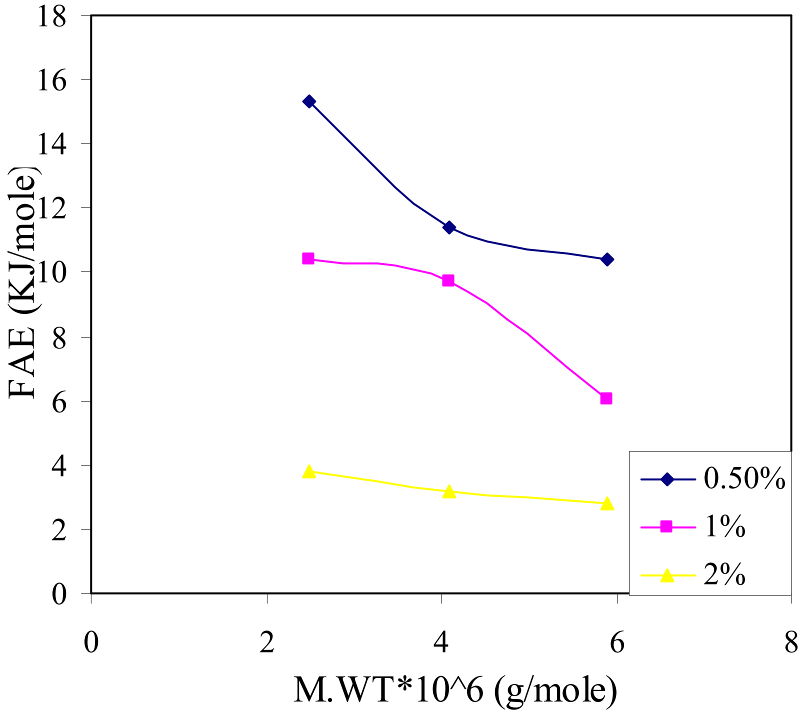


Figure 4-32 Flow Activation Energy verse Molecular Weight of Oppanol B at Different Concentration in Gas Oil

Figure 4-26, 4-28 and 4-30 show the flow activation energy decrease when increasing concentration of Oppanol B 150, 200 and 250 respectively in gas oil, these results agreed with previous literature (77), which uses other additives in asphalt binders.

Figure 4-31 shows that the flow activation energy decreases when increasing the molecular weight of Oppanol B at different concentrations in gas oil.

From Figure 4-32 it is clear that the flow activation energy decreases, when increasing the concentration of Oppanol B at different molecular weights in gas oil.

Chapter Five

Conclusions and Recommendations

5.1 Conclusions

Several conclusions have been extracted from the present work:

1- Reduced viscosity increases with increasing the concentration of polyisobutylene in crude and gas oil where the polyisobutylene in crude and gas oil behaves as neutral polymer.

2- Intrinsic viscosity of polyisobutylene in crude and gas oil decreases with increasing the temperature.

3- k and a (Mark-Houwink constants) was determined for polyisobutylene in crude and gas oil at temperature 40°C, and this has not been mentioned in the literature and could be used for unknown M.WT of the same system at 40°C.

4- Intrinsic viscosity of different molecular weight of polyisobutylene in gas oil is higher than that in crude oil at temperature 40°C.

5- When OCP (Viscoplex-4-677, Viscoplex-215496, and Lubrizol R 7077) have been dissolved in crude oil, it shows that there are two types of OCP, the first type is (Viscoplex-4-677), where its reduced viscosity increases with increasing of concentration which behaves as neutral polymer, the second types is (Viscoplex-215496, Lubrizol R7077), where the reduced viscosity increases with decreasing the concentration where it is behave as polyelectrolyte.

6- When OCP (Viscoplex-4-677) has been dissolved in crude oil, it behaves as polyisobutylene in crude oil where the intrinsic viscosity decreases with increasing of temperature, so that this type of OCP can be used in crude oil as drag reduction agent like polyisobutylene.

7- Poluisobutylene, Xanthan gum and Polyacrylamide used as drag reduction agent, show that xanthan gum behaves as polyelectrolyte where the reduced viscosity of xanthan gum increases as concentration of xanthan gum decreases, but the reduced viscosities of polyisobutylene and polyacrylamide increase as the concentration of polymers increases and they behave as neutral polymer.

8- Flow activation energy decreases with increasing concentration and molecular weight of polyisobutylene in crude and gas oil.

5.2 Recommendations

1- Estimation of intrinsic viscosity for other polymers such as polyethylene oxide, polystyrene and polymethylemethacrylate in different solvent, which is used in different industry and then classify the polymers which behave as neutral polymers or polyelectrolyte.

2- Estimation of intrinsic viscosity for those polymers at different temperatures and plot intrinsic viscosity versus temperature.

3- Study the suitability of OCP as drag reduction agent.

4- Estimation of k and a (Mark-Houwink constants) for polymers unknown in literature in order to estimate the molecular weights of those polymers.

5- Estimation of the flow activation energy for those polymers in different solvents.

6- A theoretical program for the relation of intrinsic viscosity, flow activation energy and drag reduction agent is recommended for feature work.

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Appendix A

Intrinsic Viscosity

Table A-1 Crude Oil with Oppanol B 150 Additive at Temperature 40 °C, Time of crude oil=54 sec.

Con.(w/v)	Time(sec)	$\eta_{rel}=t/t_0$	$\eta_{sp}=t-t_0/t_0$	$\eta_{red}=\eta_{sp}/conc$	$[\eta]$(100ml/g)	Slop = $k[\eta]^2$	k
0.5g/100ml	115	2.12	1.12	2.24	1.78	0.71	0.224
0.4g/100ml	102	1.88	0.88	2.2			
0.3g/100ml	88	1.63	0.63	2.1			
0.2g/100ml	76	1.4	0.4	2			

Table A-2 Crude Oil with Oppanol B 150 Additive at Temperature 100 °C, Time of crude oil=31sec

Con.(w/v)	Time(sec)	$\eta_{rel}=t/t_0$	$\eta_{sp}=t-t_0/t_0$	$\eta_{red}=\eta_{sp}/conc$	$[\eta]$(100ml/g)	Slop = $k[\eta]^2$	k
0.5g/100ml	71	2.29	1.29	2.58	1.52	2.17	0.9
0.4g/100ml	60	1.94	0.94	2.36			
0.3g/100ml	51	1.64	0.64	2.15			
0.2g/100ml	43	1.38	0.38	1.93			

Table A-3 Crude oil with Oppanol B 200 Additive at Temperature 40 °C, Time of crude oil=51 sec.

Con.(w/v)	Time(sec)	$\eta_{rel}=t/t_0$	$\eta_{sp}=t-t_0/t_0$	$\eta_{red}=\eta_{sp}/conc$	$[\eta]$(100ml/g)	Slop = $k[\eta]^2$	k
0.5g/100ml	117	2.29	1.29	2.58	2.18	1	0.22
0.4g/100ml	102	2	1	2.5			
0.3g/100ml	88	1.72	0.72	2.41			
0.2g/100ml	75	1.47	0.47	2.35			

Table A-4 Crude Oil with Oppanol B 200 Additive at Temperature 100 °C, Time of crude oil=21 sec.

Con.(w/v)	Time(sec)	$\eta_{rel}=t/t_0$	$\eta_{sp}=t-t_0/t_0$	$\eta_{red}=\eta_{sp}/conc$	$[\eta]$(100ml/g)	Slop = $k[\eta]^2$	k
0.5g/100ml	49	2.33	1.33	2.66	2.091	1.15	0.26
0.4g/100ml	42	2.03	1.03	2.55			
0.3g/100ml	36	1.72	0.72	2.43			
0.2g/100ml	31.5	1.45	0.45	2.32			

Table A-5 Crude Oil with Oppanol B 250 Additive at Temperature 40 °C, Time of crude oil=51 sec

Con.(w/v)	Time(sec)	η_{rel}=t/t_0	η_{sp}=t-t_0/t_0	η_{red}= η_{sp}/conc	$[\eta]$(100ml/g)	Slop = k$[\eta]^2$	k
0.5g/100ml	150	2.94	1.94	3.9	2.9	2	0.24
0.4g/100ml	127	2.49	1.49	3.72			
0.3g/100ml	100	2.03	1.03	3.46			
0.2g/100ml	85	1.66	0.66	3.33			

Table A-6 Crude Oil with Oppanol B 250 Additive at Temperature 100°C, Time of crude oil=21 sec.

Con.(w/v)	Time(sec)	η_{rel}=t/t_0	η_{sp}=t-t_0/t_0	η_{red}= η_{sp}/conc	$[\eta]$(100ml/g)	Slop = k$[\eta]^2$	k
0.5g/100ml	73	3.47	2.47	4.95	2.65	3	0.42
0.4g/100ml	58	2.76	1.76	4.44			
0.3g/100ml	46	2.19	1.19	4			
0.2g/100ml	36	1.71	0.71	3.58			

Table A-7 Relation of Intrinsic Viscosity with Different Molecular Weight of Oppanol B in Crude oil at Temperature 40 °C.

Molecular weight (g/mole)	Intrinsic viscosity (ml/g)	log(M.WT)	$\log[\eta]$
2.5*10^6	178	6.397	2.25
4.1*10^6	218	6.612	2.34
5.9*106	290	6.77	2.46

Table A-8 Crude Oil with Viscoplex-4-677 Additive at Temperature 40 °C, Time of crude oil=73 sec.

Con.(w/v)	Time(sec)	$\eta_{rel}=t/t_0$	$\eta_{sp}=t-t_0/t_0$	$\eta_{red}=\eta_{sp}/conc$	$[\eta]$(100ml/g)	Slop = $k[\eta]^2$	k
2g/100ml	164	2.24	1.24	0.62	0.557	0.109	0.351
1.6g/100ml	144	1.97	0.97	0.61			
1g/100ml	117	1.6	0.6	0.6			
0.6g/100ml	98	1.34	0.34	0.57			

Table A-9 Crude Oil with Viscoplex-4-677 Additive at Temperature 100 °C, Time of crude oil=24 sec

Con.(w/v)	Time(sec)	$\eta_{rel}=t/t_0$	$\eta_{sp}=t-t_0/t_0$	$\eta_{red}=\eta_{sp}/conc$	$[\eta]$(100ml/g)	Slop = $k[\eta]^2$	k
2g/100ml	49	2.04	1.04	0.52	0.379	0.06	0.44
1.6g/100ml	43	1.79	0.79	0.49			
1g/100ml	35	1.458	0.458	0.46			
0.6g/100ml	30	1.25	0.25	0.416			

Table A-10 Crude oil with Additive Viscoplex (215496) at Temperature 40 °C, Time of crude oil=51 sec.

Con.(w/v)	Time(sec)	$\eta_{rel}=t/t_0$	$\eta_{sp}=t-t_0/t_0$	$\eta_{red}=\eta_{sp}/conc$	$[\eta]$(100ml/g)	Slop = $k[\eta]^2$	k
2g/100ml	76	1.49	0.49	0.25	0.55	0.15	0.49
1.8g/100ml	77	1.51	0.51	0.28			
1.6g/100ml	76	1.49	0.49	0.31			
1.4g/100ml	75	1.47	0.47	0.34			
1g/100ml	72	1.41	0.41	0.41			
0.5g/100ml	63	1.23	0.23	0.47			

Table A-11 Crude Oil with Additive Viscoplex (215496) at Temperature 100 °C, Time of crude oil=20 sec

Con.(w/v)	Time(sec)	$\eta_{rel}=t/t_0$	$\eta_{sp}=t-t_0/t_0$	$\eta_{red}=\eta_{sp}/conc$	$[\eta]$(100ml/g)	Slop = $k[\eta]^2$	k
2g/100ml	25	1.25	0.25	0.125	0.633	0.216	0.54
1.8g/100ml	27	1.35	0.35	0.2			
1.6g/100ml	28	1.4	0.4	0.25			
1.4g/100ml	28	1.4	0.4	0.285			
1g/100ml	28	1.4	0.4	0.4			
0.5g/100ml	25	1.25	0.25	0.5			

Table A-12 Crude oil with Additive Lubrizol R7077 at Temperature 40 °C, Time of crude oil=51.

Con.(w/v)	Time(sec)	$\eta_{rel}=t/t_0$	$\eta_{sp}=t-t_0/t_0$	$\eta_{red}=\eta_{sp}/conc$	$[\eta]$(100ml/g)	Slop = $k[\eta]^2$	k
2g/100ml	73.5	1.44	0.44	0.22	0.439	0.09	0.47
1.8g/100ml	74	1.45	0.45	0.25			
1.6g/100ml	73	1.43	0.43	0.27			
1.2g/100ml	73.5	1.44	0.44	0.37			
1g/100ml	72.5	1.42	0.42	0.42			
0.8g/100ml	70.5	1.38	0.38	0.48			

Table A-13 Crude Oil with Additive Lubrizol R7077 at Temperature 100 °C, Time of crude oil=21 sec.

Con.(w/v)	Time(sec)	η $_{rel}$=t/t$_0$	η $_{sp}$=t-t$_0$/t$_0$	η $_{red}$= η$_{sp}$/conc	$[\eta]$(100ml/g)	Slop = $k[\eta]^2$	k
2g/100ml	35	1.66	0.66	0.33	0.64	0.25	0.61
1.8g/100ml	34	1.61	0.61	0.34			
1.6g/100ml	33	1.57	0.57	0.35			
1.2g/100ml	30	1.42	0.44	0.37			
1g/100ml	29	1.38	0.38	0.38			
0.8g/100ml	28	1.33	0.33	0.4			

TableA-14 Gas oil with Oppanol B 150 Additive at Temperature 40 °C, Time of gas oil= 72 sec.

Con.(w/v)	Time(sec)	η $_{rel}$=t/t$_0$	η $_{sp}$=t-t$_0$/t$_0$	η $_{red}$= η$_{sp}$/conc	$[\eta]$(100ml/g)	Slop = $k[\eta]^2$	k
0.5g/100ml	275	3.8	2.8	5.63	3.2	3.57	0.34
0.2g/100ml	134	1.86	0.86	4.3			
0.1g/100ml	101	1.38	0.38	3.86			

0.09g/100ml	94	1.3	0.3	3.4			

TableA-15 Gas oil with Oppanol B 150 Additive at Temperature 100 °C, Time of gas oil= 34 sec.

Con.(w/v)	Time(sec)	$\eta_{rel}=t/t_0$	$\eta_{sp}=t-t_0/t_0$	$\eta_{red}=\eta_{sp}/conc$	$[\eta]$(100ml/g)	Slop = $k[\eta]^2$	k
0.5g/100ml	105	3.08	2.08	4.17	2.301	5	0.94
0.2g/100ml	55	1.61	0.61	3.1			
0.1g/100ml	44	1.29	0.29	2.8			
0.09g/100ml	41	1.23	0.23	2.5			

TableA-16 Gas oil with Oppanol B 200 Additive at Temperature 40 °C, Time of gas oil= 72 sec.

Con.(w/v)	Time(sec)	$\eta_{rel}=t/t_0$	$\eta_{sp}=t-t_0/t_0$	$\eta_{red}=\eta_{sp}/conc$	$[\eta]$(100ml/g)	Slop = $k[\eta]^2$	k
0.5g/100ml	491	6.8	5.8	11	4.21	14. 28	0.8
0.2g/100ml	172	2.38	1.38	6.9			
0.1g/100ml	114	1.58	0.58	5.8			
0.09g/100ml	106	1.47	0.47	5.24			

TableA-17 Gas oil with Oppanol B 200 Additive at Temperature 100 °C, Time of gas oil= 34 sec

Con.(w/v)	Time(sec)	$\eta_{rel}=t/t_0$	$\eta_{sp}=t-t_0/t_0$	$\eta_{red}=\eta_{sp}/conc$	$[\eta]$(100ml/g)	Slop = $k[\eta]^2$	k
0.5g/100ml	220	6.42	5.4	10.9	3.03	17	1.8
0.2g/100ml	74	2.17	1.17	5.88			
0.1g/100ml	51	1.5	0.5	5			
0.09g/100ml	47	1.38	0.38	4.24			

TableA-18 Gas oil with Oppanol B 250 Additive at temperature 40 °C, Time of gas oil= 72 sec

Con.(w/v)	Time(sec)	$\eta_{rel}=t/t_0$	$\eta_{sp}=t-t_0/t_0$	$\eta_{red}=\eta_{sp}/conc$	$[\eta]$(100ml/g)	Slop = $k[\eta]^2$	k
0.2g/100ml	242	3.36	2.36	11.8	5.41	26.6	0.9
0.1g/100ml	139.5	1.94	0.94	9.4			
0.09g/100ml	131	1.819	0.819	9.1			
0.07g/100ml	111	1.54	0.54	7.73			

TableA-19 Gas oil with Oppanol B 250 Additive at Temperature 100 °C, Time of gas oil= 34 sec

Con.(w/v)	Time(sec)	$\eta_{rel}=t/t_0$	$\eta_{sp}=t-t_0/t_0$	$\eta_{red}=\eta_{sp}/conc$	$[\eta]$(100ml/g)	Slop = $k[\eta]^2$	k
0.2g/100ml	104	3.058	2.058	10.29	3.4	50	4.3
0.1g/100ml	59.5	1.75	0.75	7.5			
0.09g/100ml	56	1.647	0.647	7.18			
0.07g/100ml	47	1.38	0.38	5.46			

Table A-20 Relation of Intrinsic Viscosity with Different Molecular Weight of Oppanol B in Gas oil at Temperature 40 °C.

Molecular weight (g/mole)	Intrinsic viscosity (ml/g)	log(M.WT)	$\log[\eta]$
2.5*10^6	320	6.397	2.505
4.1*10^6	421	6.612	2.62
5.9*106	541	6.77	2.733

TableA-21 Water with XG Additive at Temperature 40 °C, Time of water= 45 sec

Con.(w/v)	Time(sec)	$\eta_{rel}=t/t_0$	$\eta_{sp}=t-t_0/t_0$	$\eta_{red}=\eta_{sp}/conc$	$[\eta]$(100ml/g)	Slop = $k[\eta]^2$	k
2g/100ml	55	1.22	0.22	0.11	0.64	0.17	0.44
1.8g/100ml	57	1.26	0.26	0.15			
1.6g/100ml	59	1.31	0.31	0.195			
1.4g/100ml	63	1.4	0.4	0.28			
1.2g/100ml	63	1.4	0.4	0.32			
1g/100ml	62	1.37	0.37	0.37			

TableA-22 Water with PAM Additive at Temperature 40 °C, Time of water= 45 sec

Con.(w/v)	Time(sec)	$\eta_{rel}=t/t_0$	$\eta_{sp}=t-t_0/t_0$	$\eta_{red}=\eta_{sp}/conc$	$[\eta]$(100ml/g)	Slop = $k[\eta]^2$	k
0.026g/100ml	111	2.52	1.52	57.3	34.9	909	0.74
0.02g/100ml	91	2.06	1.06	50			
0.018g/100ml	83	1.886	0.886	49.2			
0.013g/100ml	72	1.636	0.636	48			
0.0092g/100ml	61	1.38	0.38	41.3			

الخلاصة

تم دراسة اللزوجة الجوهرية وطاقه تنشيط الجريان لعدة بوليمرات استخدمت في بعض التطبيقات الصناعية ,بوليمرات تذوب بالمذيبات الهايدروكاربونية والتي هي البولي ايزوبيتولين عالية الوزن الجزيئي نوع (الاوبانول) حيث استخدم ثلاث انواع من الاوبانول نوع250,200,150عند اوزان جزيئية 5.9,4.1,2.5مليون غم/مول حيث اذيبت بالنفط الخام وزيت الغاز وثلاثة من أنواع الإضافات جلبت من مصفاة الدورّة وهي الاولفين كوبوليمر حيث اذيبت بالنفط الخام وايضابوليمرات تذوب بالماء والتي هي polyacrylamide عند وزن جزيئي عالي وXanthan Gumعند وزن جزيئي 3.7مليون غم/مول.

لقد اجريت قياسات اللزوجة الجوهرية وثابت هاكنز على هذة الانواع من البوليمرات المذكوره في الاعلى عند درجه حرارة 40و100 درجة سيليزية باستخدام capillary viscometer .

لقد وجد ان اللزوجه الجوهرية للبولي ايزو بيوتلين تنخفض عند ارتفاع درجة الحرارة في النفط الخام وزيت الغاز وهناك نوع من انواع الاولفين كوبوليمر يتصرف نفس تصرف البولي ايزو بيوتلين حيث يمكن استخدامة كعامل مقلل للاعاقة.
تم حساب Mark-Houwink parameter (k and a) للبولي ايزو بيوتلين في النفط الخام يساوي0.0442و 0.558 وفي زيت الغازيساوي 0.0415و0.6 عند درجه حرارة40 درجة سيليزية وانها لم تذكر سابقا .

لقد لوحظ ان هناك نوعين من البوليمرات التي استخدمت كعامل مقلل للاعاقة، بوليمرات متعادله كبولي ايزو بيوتلين وبوليمرات متأينه مثل Xanthan Gum حيث وجد ان البوليمرات المتأينة تسلك سلوك يختلف عن البوليمرات المتعادله حيث ان reduced viscosity تزداد كلما قل تركيز البوليمر.

لقد وجد ان طاقه التنشيط الجريان تقل عند اضافة البولي ايزوبيوتلين بالنفط الخام وزيت الغاز.

شكر وتقدير

وأنا أضع قلمي بعد أن أنجزت هذا البحث لايسعني إلا أن أشكر كل من وقف وراء هذا الانجاز بعد شكر الله تعالى

ويشرفني أن أتقدم بجزيل الشكر والعرفان الى أستاذي الفاضل الدكتور **طالب بهجت كشموله** لما أبداه لي من جهد في التوجية والارشاد والمتابعة فجزاءه الله عني خير جزاء

وأود التقدم بالشكر الى السيد رئيس القسم المحترم وكافة منتسبي القسم ممن كان له الفضل في أتمام هذا البحث

اود ايضا ان اشكر جميع منتسبي **مصفى الدورة ووزاره العلوم والتكنولوجيا** لابدائهم المساعده في السماح لي ان اعمل في مختبراتهم

كما أوجه شكري وتقديري الى زملائي طلبة الدراسات العليا جميعا وكل من أنار دربي لأصل إلى هذه المرحلة

و أقدم شكري الى من ذكر اسمه يشرفني وصورته لا تبرح عن ذاكرتي الى اول من ادبني وعلمني وغرس فيه حب التعلم ,**ابي رحمه الله**

كما اشكر والدتي التي طالما سهرت الى جانبي و لولاها لا اصل الى هذه المرحله

وأخيرا أقدم شكري الى جميع عائلتي الذين كانوا خير سند لي في تذليل العقبات لي

رباب عماد الجبوري

دراسة اللزوجة الجوهرية وطاقه تنشيط الجريان لبعض البوليمرات في مختلف المذيبات

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

من قبل
رباب عماد احمد الجبوري
بكالوريوس علوم في الهندسة الكيمياوية 2008

جمادى الاول 1432
نيسان 2011