DISSOLVING AND TESTING OF DRAG - REDUCING HIGH MOLECULAR WEIGHT POLYMERS

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Chemical Engineering

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Abstract

Throughput increase by drag-reducing additives offers a suitable quick solution to meet increased demand by pipelining of oil or water which arises either permanently or seasonally. This has placed increased emphasis upon studies directed towards preparing efficient solutions of drag- reducer additives. Commercially available polyisobutylenes (Oppanol B types) of three different high molecular weights in addition to water soluble carboxymethylcellouse were chosen for the investigation. Five locally produced, different oil products, namely light naphtha, heavy naphtha, reformate, special spirit and xylene mixture, were tested as solvents for polyisobutylene polymers.

It was found that reformate was considered the best solvent for Oppanol B type polymers. Homogenous and effective 2 wt. % polymeric solutions were obtained at room temperature by using a shaker for one to three days according to their molecular weight. A homogenous 4 wt. % CMC solution in water was prepared after one day of shaking.

Drag reduction efficiency of polyisobutylenes with three different molecular weights ($2.6*10^6$ g/mole, $4.1*10^6$ g/mole and $5.9*10^6$ g/mole) were tested as a function of polymer concentration and flow rate in a gas oil turbulent flow produced in a gear pump. It was observed that the additive effectiveness was a function of concentration, Reynolds number (turbulence) and the molecular weight of the polymer. Oppanol B 250 of $5.9*10^6$ g/mole molecular weight is the most effective additive.

Friction factor was calculated from the experimental data. For untreated gas oil, friction factor values lie near Blasuis asymptote. While, by the addition of polymers into the flow, the friction values are positioned towards Virk asymptote.

Carboxymethylecellouse shows a lower effectiveness as a drag-reducer by pipelining of water. This probably due to its lower molecular weight and its molecular structure compared with Oppanol B polymers of high molecular weight and linear, flexible structure.

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Variables Notations

A	Area	[m^2]
C	Polymer concentration	[ppm]
c_m	Mass concentration	[g/mole]
D	Pipe diameter	[m]
%DR	Percentage drag reduction	[-]
f	Fanning friction factor	[-]
f_b	Friction factor of polymer solution	[-]
f_s	Friction factor of solvent	[-]
ID	Inside Diameter	[m]
K	Mark-Houwink parameter	[cm^3/g]
Le	Entrance length	[m]
L	Testing section length	[m]
M, Mw	Molecular weight	[g/mole]
M_V	Average molecular weight	[g/mole]
m	Mass	[g]
NDe	Deborah number	[-]
ΔP	Pressure drop	[N/m^2]
Q	Volumetric flow rate	[m^3/hr]
Re	Reynolds number	[-]
R_G	Radius of gyration	[m]
r	Radius of tube	[m]
T	Temperature	[K]
t	Flow time	[sec]
%TI	Percentage throughput increase	[-]
U	Solution velocity	[m/s]

V	Specific Volume	[-]

Abbreviations

BHT	Butylated hydroxyl toluene
CDR	Connoco drag reducer
CMC	Soduim Carboxymethylcellulose
CTAC	Cetyl tri-methyl ammonium chloride
DR	Drag Reduction
DRA	Drag Reduction Agent
FDA	Food Drug Administration
FRA	Friction Reduction Agent
GG	Guar gum
HEC	Hydroxyethylecellulose
LM	Low molecular weight
NaCl	Sodium Chloride
PAM	Polyacrylamide
PCIP	Polycis-isoprene
PDMS	Polydimethylsiloxane
PEO	Polyethylene oxide
PIB	Polyisobutylene
PMMA	Polymethyl methacrylate
PS	Polystyrene
rpm	Revolution Per Minute
TAPS	Trans Alaska Pipeline System
VAMW	Velocity Average Molecular Weight
XG	Xanthan gum

Greek Letters

ρ	Fluid density	[kg/m^3]
μ	Dynamic viscosity	[poise]
τ_1	Relaxation time	[sec^{-1}]
φ	Volume fraction of sphere	[-]
ν	Kinamatic viscosity	[centi stock]
β	Viscometer constant	[centi stock/sec]
$[\eta]$	Intrinsic viscosity	[poise]
L	Length of tube	[m]
η_{sp}	Specific viscosity	[-]
$\eta_{\circ}$	Viscosity of pure solvent	[poise]
α	Thermal expansion coefficient	[K^{-1}]
α	Mark-Houwink parameter	[-]

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Chapter One

Introduction

1.1 Introduction

A large amount of energy loss due to friction occurs in many cases of turbulent flow, generally. However, it is well known that turbulent drag reduction (DR) which is drastic reduction of frictional resistance can be easily observed by dissolving a minute amount of long-chain polymer molecules in water or in organic solvents in a turbulent flow (Kulick and Kotter1989). Polymer solutions undergoing a turbulent flow in a pipe thereby require lower pressure drop to maintain the same volumetric flow rate. The addition of small amounts of additives to the flowing fluids can show significant effects on a lot of flow, transition to turbulence, vortex formation and break-up (Sreenivasan and White 2000).

The drag reduction effect is extremely interesting from a particular point of view. Liquids are mostly transported through pipes, and drag reduction by adding a small amount of polymers can offer large economic advantages and a larger effectiveness of this transportation. Iraq is considered one of the main countries exporting oil through a net work of pipelines. Considerations of throughput increase usually arise in such countries to meet increased demand, which can be either being permanent or seasonal. Drag reducing additives offer the best quick, temporary solution to such a problem. Its main advantage is that no capital investment is involved (Thomas et.al 2005).

In addition to these practical considerations, the phenomenon of drag reduction by polymer additives is very interesting from a fundamental fluid dynamics point of view as well. The fact that such small changes in the fluid can so drastically alter the turbulent flow characteristics strongly hints at the existence of a key mechanism of turbulence momentum transport with which the polymer interferes. Furthermore the study of polymeric drag reduction could help in gaining more knowledge about the turbulence itself (Thomas et.al 2005).

The physical mechanism responsible for the drag reduction required to consider the turbulence processes that are present in the flow, and the influence of the rheological properties of the fluid, as well the rheological characteristics of these solutions are not only quite complex, but they are generally difficult to evaluate quantitatively because of low concentration of polymer solution. These properties coupled with the complex character of turbulent flow, resulted in an exceedingly complex system which is virtually difficult to analysis precisely. Consequently, various approximations and simplifying assumptions are necessary in order to obtain a relationship between observable quantities (Gowarijer et.al 1987).

Polymers fluids are called viscoelastic fluids. This means that the fluid has both viscous and elastic properties. Maxwell (Bewersdoff 1984) assumed that the application of a stress to the fluid causes some ordinary elastic deformation flowed by a newtonian type of viscous.

Effective polymeric Drag- reducing additives are considered to be flexible, linear with a high molecular weight such as Polyisobutylene (Choi and Jhon 1996). The dependence of drag reduction efficiency is known to be a function of polymer molecular weight; polymer concentration and the degree of turbulence. The additives undergo undesirable mechanical and chemical degradation under turbulent flow and rotation speed. Longer linear molecules are more susceptible to degradation (Rho 1996).

This has placed increased emphasis upon studies directed towards preparing an effective locally produced polymer solution. Thus, the feasibility of preparing a suitable polymer solution, using some locally produced solvents, assumes greater importance, since dissolving of high molecular weight polymers is very complicated because the polymer molecule is a giant molecule compared to solvent molecules and is made up hundreds of chain segments, the large size and coiled nature of the polymer molecules and also because of strong forces of attraction between them. Solvent molecules take time to establish interactions with polymer molecules and care should be taken to avoid the degradation of polymer by stirring, light and others (Gowarijer et.al 1987).

1.2 Aim of the Work

The present study was aimed at applying state-of-the art knowledge to select the most suitable solvents and conditions to dissolve high molecular weight, straight chain drag-reducing polymers. Hydrocarbon Soluble polyisobutylenes, with three different high molecular weights, namely Oppanol types, 150, 200 and 250 were chosen for this investigation. Furthermore, sodium carboxymethylcellose, as water soluble polymer was also included in this study. Viscosity and density of polymeric solutions were measured at different temperatures and concentrations.

Further objective of the present investigation was to evaluate the drag-reducing effectiveness of the considered additives in a laboratory circulation loop using gas oil and water as the flowing liquids.

Chapter Two

General Part

2.1 Drag Reduction in Pipe Flow

Turbulent pipeline flow consists of three regions across the pipe diameter: the laminar sub layer, the buffer region, and the turbulent core as shown in figure (2.1) (Thomas et.al. 2005). Fluid near the pipe wall (the laminar sub layer) tries to stay stationary while fluid in the center region of the pipe (the turbulent core) is moving quickly. This large difference in fluid velocity between the laminar sub layer and the turbulent core causes turbulent bursts to occur in the buffer region. Turbulent bursts propagate and form turbulent eddies, which cause inefficiencies in the hydraulic energy that drives the fluid down the pipeline.

The net result of using a drag-reducing polymer in turbulent flow is a decrease in the frictional pressure drop in the pipeline. Turbulence and the resulting frictional pressure drop have been shown to be reduced by as much as 70% with drag-reducing polymers (Thomas et.al. 2005).

Drag reduction is defined as the difference in frictional pressure drop along a segment of pipeline comparing untreated fluid and fluid containing drag reducer at a constant flow rate. It can be calculated using equation (2.1), where $\Delta P_{\text{untreated}}$ is the pressure drop in the pipeline with no drag reducer present, and $\Delta P_{\text{treated}}$ is the pressure drop in the pipeline with drag reducer present. Equation (2.1) assumes the flow rate is constant.

$$\%DR. = \frac{\Delta P_{untreated} - \Delta P_{treated}}{\Delta P_{untreated}} * 100 \qquad \ldots \quad (2.1)$$

For two-phase and multiphase slug or bubble flow applications, the continuous liquid phase is the phase which can be drag-reduced. For example, a water content greater than 50 volume percent in the liquid phase makes a water-continuous phase and thus requires a water soluble drag reducer as opposed to a hydrocarbon soluble drag reducer. Water soluble drag reducers are often used in water flooding operations, high water-cut production lines, spent water disposal, and transport of oily water.

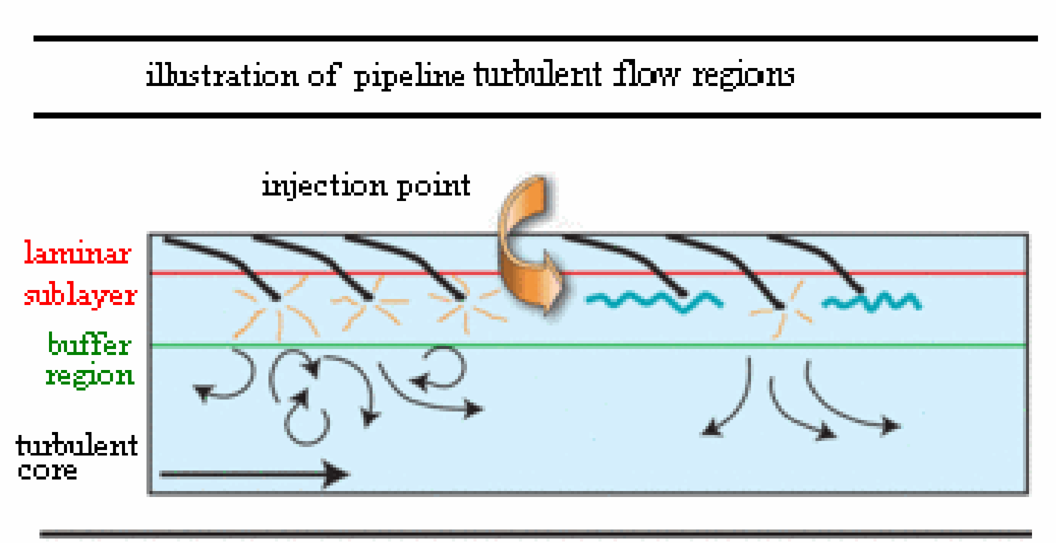


Fig. (2.1) Drag reduction occurs due to suppression of the energy dissipation by turbulent eddy currents near the pipe wall during turbulent flow.

Recently, the use of flow improvers took a step further into the offshore environment and multiphase applications. Flow improvers can be used to manage and increase production, significantly lower discharge pressure, and in some instances, change the flow regime, and improve operations (Thomas et.al 2005).

2.2 Advantages of Drag Reduction

The drag reduction effect is extremely interesting from a particular point of view. Liquids are mostly transported through pipes, and a drag reduction by adding a small amount of polymers can offer large economic advantages and a larger effectiveness by this method of transportation. The most spectacular success in polymer applications for drag reduction has been the use of oil-soluble polymers in the trans-Alaska pipeline system, where as a result the flow rate has been increased by 32,000 m^3/d (Sarah 1990).

In addition to drag reduction, the polymer also causes a reduction in heat transfer, which is advantageous in maintaining low oil viscosity (Hoyt 1990). A similar application is the addition of polymers to oil being pumped from offshore platforms to shore facilities (Beaty et al. 1984). Also, in sewage pipes and storm-water drains polymers have been used to increase the flow rates so that the peak loads do not result in overflowing; if only relatively infrequent use is required, this can be much cheaper than constructing new pipes (Sellin 1988). Another application is the increase in the range and coherence of water jets from firefighting hoses, but this idea has not been widely exploited (Fibula 1971). A military application which has been patented is the reduction of the drag acting on a torpedo by ejecting a sea-water-polymer solution from the torpedo nose (Fabula et al 1980). Finally, we mention a possible medical application: the addition of low concentrations of polymers might be capable of improving blood flow through stenotic vessels without altering flow through normal vessels, as was suggested by a study by Unthank et al. (1992).

2.3 Drag Reducing Additives

Drag reduction has been reported for several solvents/additives system, including dilute solution of high molecular weight, soluble polymers, surfactants and micellar system. Suspension of insoluble particles such as fine grains or fiber, and polymer solutions mixed with soaps or fibers considered to be also as drag-reducing agents (Virk 1975).

It has also been found that modified surface such as complaint surfaces, heated surfaces, and surfaces covered with riblets (small triangular ribs) aligned with the flow, can provide drag reduction of a varying degree (Morgan 1990).Table (2.1) (Virk 1975)summarizes the main drag reducing polymers.

Table (2.1) Drag Reducing Polymers

Water soluble	Hydrocarbon soluble
Polyacrylamide (PAM)	Polyisobutylene (PIB)
Polyethyleneoxide (PEO)	Polyethyleneoxide (PEO)
Guar gum (GG)	Polymethylmethacrylate (PMMA)
Xanthan gum (XG)	Polydimethylsiloxane (PDMS)
Soduim Carboxymethylcellulose (CMC)	Polycisisoprene (PCIP)
Hydroxyethylecellulose (HEC)	Polystyrene (PS)

Polyethyleneoxide (PEO) has been the most widely studied for both laboratory and commercial application, including fire fighting and marine propulsion. PEO is flexible, linear with a high molecular weight; its utility in multiple pass application is limited due to its extreme sensitivity to shear degradation. Drag reduction similar to that obtained in water has been shown for PEO in other solvents such as, sea water, plasma, benzene, dioxin, and chloroform. Mixed PEO systems such as PEO graft polymer, polymer/soap and polymer/dye mixture have shown to provide varying levels of drag reducing agent (Morgan 1990).

Polyacrylamide PAM is the other synthetic water soluble and differs from PEO in that it has a side chain and is less susceptible to shear degradation. The related polymer, polyacrylic acid can be formed by hydrolysis of PAM. Most of the laboratory and commercial studies, however, have focused on PEO and PAM due to their availability, their relatively low cost, and the large body of previously reported experiments describing their solution behavior available in the literature (Morgan 1990).

One of the most widely used commercial drag reducing biopolymer is guar gum (GG) which is a plant polysaccharide with a semi rigid backbone. It has been used for a number of years in oil field application, and in the petroleum industry where its friction reducer agent was discovered (Oustehout and Hall 1960). The major limitation of guar gum in drag reduction application is its susceptibility to biodegradation. It has been shown that resistance to shear and biodegradation can be increased by grafting acrylamide to guar gum molecules (Singh and Kumer 1985).

Modified cellulose compounds such as Sodium Carboxymethylcellulose (CMC) was the first water-soluble polymer whose drag reducing efficiency was reported in the literature. The most widely used organic polymers are the semi-synthetic gums produced by chemical modification of cellulose. Cellulose comprises the greater part of the cell walls of plants (e.g., cotton fiber is over 90 % cellulose).

Sodium Carboxymethylcellulose is a water-soluble, colorless, odorless and nontoxic powder. It is consider as an anionic polymer. Three grades of CMC are available; low viscosity, medium viscosity, and high viscosity.

The viscosity of CMC solutions decreases and increases reversibly with the raising and lowering of temperature, but no permanent change occurs unless the solutions are kept at high temperature for a considerable length of time. CMC suspensions are shear thinning; they have high apparent viscosity at very low shear rates (Nada 1989).

The water-dispersible cellulose polymers are made by chemical modification of water insoluble cellulose, which furnishes the polymeric backbone. Although the basic unmodified cellulose chain is composed of repeating anhydroglucose rings, each of which has three hydroxyl groups capable of substitution fibrous cellulose is a complex structural mixture of crystallites and amorphous material (Nada 1989).

Consequently, in the preparation of cellulose derivatives, a single cellulose chain will show differences in availability to reaction depending upon the structure, and the substitution will not be uniform (Nada 1989).

The other biopolymer which has been widely used as a commercial drag reducer is xanthan gum (XG). XG is an intracellular polysaccharide produced by the bacteria xanthomnas. XG shows variable Rheological behavior with change in the solvent ionic strength, flow rate, and polymer concentration. Kenis has demonstrated greater shear stability for XG than for a number of other drag reducing molecules (Ambari and Deslouis 1984). The shear stability, and resistance to shear degradation decreased as follows: PAM > XG > PEO > GG.

Composition of XG polymer shows that the polymer repeats unit contains five D-glucose rings as the polymer backbone and two side chains composed of a total of six member rings. Molecular weight of xanthan gum is estimated to be about $5*10^6$ g/mole (Nada 1989).

Surfactants (Surface-Active Agents) are chemical compounds known as surfactants, which are, constituted of hydrocarbon portion (tail) and polar (or ionic) portion (head), as shown in figure (2.2)(Myers 1988). The hydrocarbon portion, which can be linear or branched, interacts very weakly with water molecules in an aqueous environment. This chain is usually called hydrophobic group. The polar (or ionic) portion of the molecule, usually called as head-group, interacts strongly with water via dipole-dipole or ion-dipole interactions. Consequently, the head group is said to be hydrophilic group (Swisher 1970).

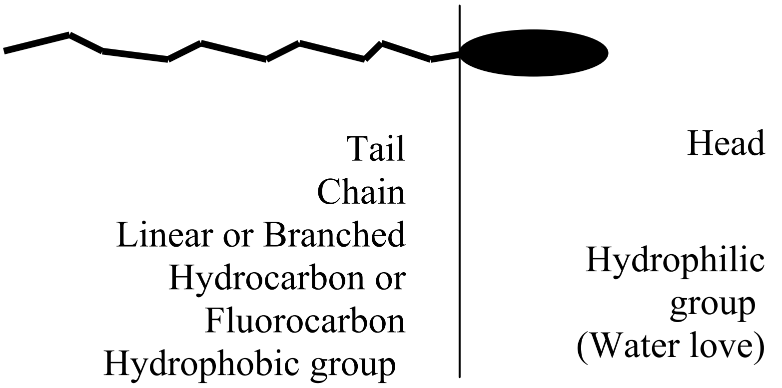


Fig. (2.2) The Basic Chemical Nature of Surface-Active Molecules

A solution of surfactant of high enough concentration to form aggregates are called micelles, which are observed to cause drag reduction in turbulent flow of gasoline (Myseles 1949) and of water (White 1967) and (Warholine et.al 1999). A remarkable observation is that drag reduction approaching 80% can be realized when the composition is such that rods like micelles are formed (Zheng et.al 2000).

Certain anionic, cationic, nonionic and also zwitterionic surfactants are considered powerful drag reducers in turbulent flow in pipes and can hence contribute to significant energy savings. Their drag reduction ability at low concentrations, as a few mill molar, is ascribed to the rod-like micelles presenting the solution. These micelles play a dominant role in the mechanisms of turbulence suppression and in the significant friction decrease which can be even higher than some high polymer solutions (Myska et.al 2001).

Micellization is the formation of a particle micelle as a result of the aggregation of single molecular or monomer of the type of surface active agents when dissolved in water. The structure shown in figure (2.3) is such that hydrocarbon chains are inside the micelle, remote from the solvent, and the polar head groups are on the outside boundary of the spherical micelle (Swisher et.al 1970).

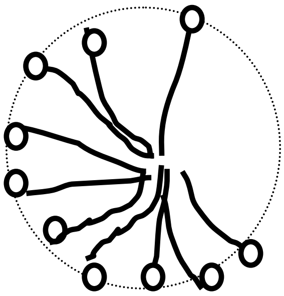
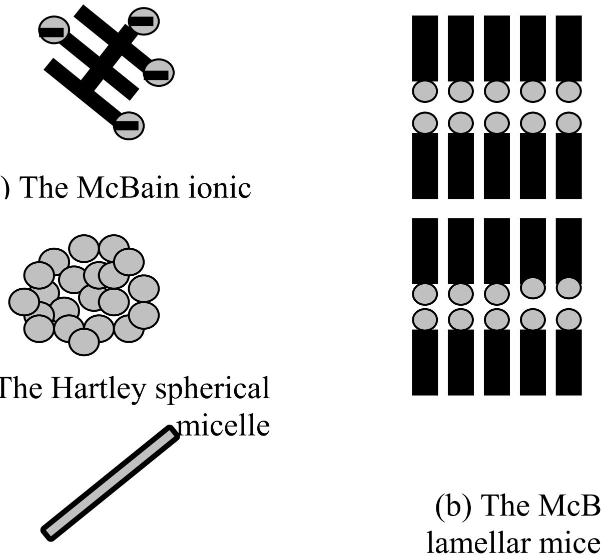


Fig. (2.3) Suggested Structure of a Cross-Section of a Spherical Micelle.

Increments of surfactant also dissolve to form separate molecules or ions up to a certain point, known as the critical micelle concentration. Beyond this point the concentration of single molecules remains relatively constant. Size and shapes of micelles can be determined by various physico-chemical means, depending on factors such as the chemical nature and architecture of the surfactant, the salt content of the solution and the temperature. They may be spheres, ellipsoids, or cylinders, as shown in figure (2.4) and may average tens or hundreds of molecules per micelle (Myers 1988).



(a) The McBain ionic

(c) The Hartley spherical micelle

(b) The McBain lamellar micelle

(d) The cylindrical micelle

Fig. (2.4) Some Suggested Classical Structures for Simple Micellar Aggregates

2.4 Polyisobutylenes (Oppanol)

2.4.1 Types and Applications

Polyisobutylenes are highly olefin hydrocarbon polymers, composed of long, straight chain macromolecules containing only chain- end olefin bonds. This molecular structure leads to chemical inertness and resistance to chemical or oxidative attack, and solubility in hydrocarbon solvents. All grades of polyisobutylene are a mixture of molecules of various sizes. The “molecular weight” of Vistanex PIB ordinarily means the viscosity average molecular weight (VAMW).

There are many types of polyisobutylenes and they can be classified according to its molecular weight and its trade name. Several types of polyisobutylene are produced by BASF Co., Germany and delivered under the marketing grad "Oppanol-B" as listed in table (2.2) (BASF 2003).

The special properties of PIB – its impermeability to gases, chemical inertness, solubility in hydrocarbon solvents, solutions of PIB have non newtonian behavior , and the physical strength of the very high-molecular-weight and FDA (Food and Drug Administration) approval in many applications – lead to a very broad range of applications in commerce, suggested by the list below (Exxonmobil 2005).

- Adhesives
- Binders and coatings
- Caulking and sealing compounds
- Chewing gum base
- Drag reducer
- Pipe wrap
- Wax blends
- Polyolefin blends
- Grease and oil additives
- Uncured sheeting
- Viscosity modifier for solutions
- Electrical and cable insulation
- Puncture-sealing compounds
- Mechanical goods

Table (2.2) Types of PIB, Oppanol-B

Oppanol B	Consistency	Weight average Mw (g/mole)	Viscosity average VAMW	Area of application
10 SFN	Soft , resinous	36 000	40 000	Chewing gum
11 SFN		46 000	49 000	
12 SFN		51 000	55 000	
13 SFN		60 000	65 000	
15 SFN		75 000	85 000	
10 N	Soft, resinous	36 000	40000	Sealant, adhesives, chewing gum, lubricant, upgrading waxes and bitumen
12 N		51 000	55 000	
15 N		75 000	85 000	
30 SF		200 000	200 000	Chewing gum, sealants, adhesives
50		340 000	400 000	Sealants, adhesives, chewing gum
50 SF		340 000	400 000	Chewing gum
80	Rubber-like	750 000	800 000	Sealants, adhesives, anti-misting
100		1 100 000	1 100 000	
150		2 600 000	2600 000	
200		4 100 000	4 000 000	Drag reduction, oil spills
246/250		>5 900 000	>5 900 000	

2.4.2 General Properties

The polyisobutylene products are light colored, odorless, tasteless and nontoxic. Vistanex LM (low molecular weight) of Exxonmobil Chemical Company and BASF are leading global suppliers of the medium and high molecular weight polyisobutylene under trade name Oppanol B types. Polyisobutylene of high molecular weight, such as Oppanol B types, are tough elastic solids. Because PIBs are essentially saturated hydrocarbons they are more resistance to heat, light, and chemical attack.

The deformation of PIB under load is strongly dependent on temperature and time. Elastic recovery of Vistanex PIB from deformation, whether compression or extension, and permanent deformation depend on the molecular weight of the polymer. The higher polymers are stiffer and more elastic, resisting deformation and permanently set more than the low molecular weight polymers.

Chemically, the various grades of Vistanex polyisobutylene behave like typical paraffinic hydrocarbons. They are generally resistant to acids, alkalis, oxygen, ozone, etc., and are, in fact, often added to other polymers to improve their resistance to chemical attack .Vistanex PIB is attacked by strong oxidizing agents such as hot nitric acid, by halogens which react by substitution to give halogenated polymers, and it will burn once ignited.

Vistanex polyisobutylenes are highly resistant to penetration by water vapor and gases, and often are added to other polymers to reduce their permeability. The higher the molecular weight of polyisobutylene, the lower its permeability. At room temperature, the nitrogen permeability of polyisobutylene is only about one-thirtieth that of natural rubber (Exxonmobile 2005).

PIBs are very stable polymers under normal conditions of use, but they can be degraded or depolymerized by heat, mechanical shear, ultra violet radiation and some chemicals such as organic peroxides.

2.5 Polymeric Solutions

2.5.1 Dissolving

Oppanol B types are generally soluble in non polar hydrocarbon solvents and insoluble in polar solvents. They are soluble in aliphatic hydrocarbons, carbon disulfide and halogenated solvents. Solubility generally decreases with increasing molecular weight of the polymer and increasing size of the aliphatic portion of the solvent molecules. Oppanol B type generally is not soluble in the common alcohols, esters, ketones, ethers, or in low-molecular –weight oxygenated solvents (Exxonmobile 2005).

As soon as the solvent and solute are brought together, the solvent molecules surround the solute molecules, establish solvent-solute interaction and break the solute-solute attraction. As this happens, the solute molecules, which are discrete, are isolated from the solid phase and, as their size is comparable to that of the solvent molecules, they diffuse fast in the solvent phase.

A polymer molecule on the other hand, is a giant molecule when compared to solvent molecules and is made up hundreds of chain segments. These long molecules, moreover, are not in the form of tightened folded random coils. Individual molecular coils are also not discrete and separate, but are interpenetrating and entangled with one another. There are also varying degree of cohesive and attractive forces between different segments of the same molecular coil as well as neighbouring coils. Forces such as dispersion, induction, dipole-dipole interaction and hydrogen bonding hold the molecular coils and their segment together tightly (Gowarijer et. al 1987).

Because of the large size and coiled nature of the polymer molecules and also because of strong forces of attraction between them, solvent molecules take time to establish interactions with polymer molecules, to overcome the force of attraction, to release individual molecules out of the chain entanglement and get them out of polymer phase. This explains the difference in the dissolution behavior of low and high molecular weight substances.

The first stage in polymer dissolution is characterized by a slow penetration of the solvent molecules into the interstices of the polymer coil and forcing them to swell. During this swelling stage the volume of the polymer matrix increases and the solvent molecules leave the solvent phase and diffuse into the polymer matrix. The polymer molecules, on the other hand, remain within the matrix itself and do not diffuse out.

The phenomenon of swelling depends purely on the forces of interaction between solvent molecules and polymer segments and is not influenced by stirring or agitation. The process can, however, be hastened by exposing more polymer area to solvent interaction. It is for this reason that in order to dissolve a polymer, it is put in the solvent in as many small pieces as possible and left overnight for swelling to occur. As swelling continues, more segments of the polymer are dissolved and loosened out. When all segments are dissolved, the molecules as a whole, in the form of a loose coil, separates out from the swollen polymer. The loosened polymer molecule then diffuses slowly out of the polymer phase and disperses in the solvent phase, forming the solution (Gowarijer et. al 1987).

2.5.2 Solution Viscosity

Fluids resist usually a flow gradient. The resistance produces a frictional force known as a viscous force proportional to the area of contact, A, between the flowing regions and to the velocity gradient, dv/dx. The constant of proportionality is called the coefficient of viscosity, η, as given in equation (2.2)

$$F = \eta \mathrm{A}\, dv/dx \qquad \ldots(2.2)$$

The unit of viscosity is a poise, 1 gm cm^{-1} s^{-1} = 10^{-1} kg m^{-1} s^{-1}. To measure viscosity, one must determine flow in the presence of a velocity gradient. A convenient way is by measuring the flow through a tube, where the flow varies across the diameter of the tube because of viscous forces. Poiseuille derived a formula for the volume, ΔV, of an incompressible fluid of viscosity, η, moved through a tube of length l and radius, r, in a time, Δt, subject to a pressure drop, ΔP, as given in equation (2.3).

$$\frac{\Delta V}{\Delta t} = \frac{\pi r^4}{8\eta l}\Delta \mathrm{P} \qquad \ldots(2.3)$$

A more accurate formula is available for compressible materials, this equation is often sufficient for measurements made in which the pressure drop is not too great (Noggle 1996). From this equation, one sees that a measure of the time it takes a specific volume to move through a tube, usually with a diameter of no more than a few millimeters, under a constant pressure drop is a direct measure of the viscosity. The time t takes a specific volume, V, to flow at a rate dV/dt is given by equation (2.4)

$$t = \frac{V}{dV/dt} \qquad \ldots(2.4)$$

Obviously, Poiseuille's formula can be used with this time measurement to determine the viscosity of a fluid, provided the other parameters are known.

Rather than a pressure drop as the driving force, many viscometry experiments use the force of gravity to drive the fluid through the tube. ρ is the density of the fluid; in g/cm^3.

$$F = \rho V_{\circ} g \qquad \ldots(2.5)$$

Under this set of conditions, equation (2.4) may be rewritten as a relation between the time and the viscosity coefficient:

$$\eta = \frac{B}{\rho} t \qquad \ldots(2.6)$$

Separate measurements of the flow time of a known volume of material and its density enable one to calculate the coefficient of viscosity. The viscometer constant, B, is theoretically related to parameters of the experiment in a similar manner to the derivation of Poisiueille's equation, but it is generally treated as a calibration parameter that is determined by measurement of the flow time of some standard material whose density and viscosity are well known.

There are many different other ways to measure viscous behavior systems. Flow viscometry, as is done in this study, is only one. Another measurement of viscosity relies on Stokes Law, which relates the drag on a falling object to the viscosity of the medium through which it falls, falling-ball viscometry. There are many other ways to measure viscosity, but they all rely on measuring the viscous force on a moving object and so require the movement of some object relative to the fluid or vice versa (Noggle 1996).

2.5.3 Viscosity of Dilute Polymer Solutions

When solvent molecules move through the polymer, the solvent receives resistance. The difficulty to flow is expressed by a quantity called viscosity, η. The higher the viscosity, the more difficult to move around, the viscosity of dilute polymer solution depends on:

- The nature of the polymer and the solvent.
- Concentration of the polymer.
- Molecular weight.
- Temperature
- Pressure.
- Shear rate.

Solution properties depend not only on the nature of the materials mixed, but on the amount of each present in the mixture, as Eyring's theory shows. A particularly important example is the viscosity of a solution of a polymeric material in a small-molecule solvent. The basis for explaining the concentration dependence of the viscosity of a polymer solution is Einstein's relationship for the viscosity of a dilute solution of spherical particles:

$$\frac{\eta}{\eta_\circ} = 1 + 2.5\phi. \qquad \ldots(2.7)$$

η is the viscosity of a solution of volume fraction, φ, of the spheres. $\eta_\circ$ is the viscosity of the pure small-molecule solvent. For particles of other shapes, a similar relationship occurs, but the numerical coefficient of the volume fraction is different. It is usual to define the specific viscosity, η_{sp} of a polymer solution by equation (2.8)

$$\eta_{sp} = \frac{\eta - \eta_{\circ}}{\eta_{\circ}} \qquad \ldots(2.8)$$

The specific viscosity is the fractional increase in the viscosity over that of the pure solvent caused by the addition of the polymer. According to the Einstein relation, equation (2.9), for a theoretical solution of perfect spheres, the specific viscosity is can be related to the concentration:

$$\eta_{sp} = \frac{10\pi r^3}{3m} c_m . \qquad \ldots(2.9)$$

r is the radius of the "spherical" molecule, m is its mass, and c_m is the mass concentration. Thus, by this simple theory, the specific viscosity is predicted to be linear in mass concentration.

For real polymer solution, the dependence of the specific viscosity on mass concentration is often more complex than this simple theory predicts. To parameterize the concentration dependence of specific viscosity, one defines the intrinsic viscosity, $[\eta]$ as:

$$[\eta] = \lim_{cm \to 0} \frac{\eta_{sp}}{c_m} \qquad \ldots(2.10)$$

Like other parameters extrapolated to infinite dilution, the intrinsic viscosity describes the interaction of a single average polymer molecule with solvent. For a spherical molecule, $[\eta]$should be proportional to the molecular volume. For many synthetic polymers in dilute solution, the chains tend to adopt a tight, ball-like configuration in solution, the average structure of which is defined by a radius of gyration R_G. For such molecules, one predicts that:

$$[\eta] = K' \frac{R_G^3}{M} \qquad \dots(2.11)$$

Where M is the molar mass and K′ is a constant. For a polymer that adopts a random-coil conformation, theory predicts that $R_G \propto M^{1/2}$. Thus, one predicts the dependence of intrinsic viscosity on molar mass of the form:

$$[\eta] = KM^{1/2} \qquad \dots(2.12)$$

This generally applies to polymer solutions under what are known as theta conditions (Flory 1953). In practice, one can describe the dependence more accurately by the empirical Mark-Houwink equation:

$$[\eta] = KM^{\alpha} \qquad \dots(2.13)$$

Where K and α are two parameters that depend on the solvent, polymer, and temperature. Values of these coefficients for several polymers and solvents are given in table (2.3) Once K and α are known for a combination of polymer and solvent, one may use the intrinsic viscosity to give the viscosity-average molar mass of a material, Mv (Brandrup and Immergut 1975).

Table (2.3) Mark-Houwink Parameters for Various Polymers and Solvents

Polymer	Solvent	Temperature/°C	K/(cm^3/g)	α
Polyisobutylene	Benzene	25	0.083	0.53
	Toluene	25	0.087	0.56
	Cyclohexane	25	0.040	0.72
	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
Polyethyleneoxide	Water	30	0.00875	0.79
	Benzene	30	0.0397	0.686

2.5.4 Stability

In common with most other high polymers, polyisobutylene with high molecular weight is degraded by heat, oxygen, shear forces and ultraviolet radiation leading to reduce its average molecular weight by these agencies (BASF 2003).

Oxidation is apparently the most active of these since inclusion of stabilizers in PIB will prevent molecular-weight degradation for a long time, even at high temperatures and under severe mechanical working. Certain organic peroxides, such as ditertiary-butyl peroxide, accelerate the depolymerization of PIB, as shown by data in table (2.4) (Exxonmobil 2005).

Table (2.4) Peroxide-Catalized Breakdown of PIB during Milling at 138°C (280°F)

Viscosity Average Molecular Weight			
Wt.% Ditertiary Butyl Peroxide:			
Milling Time minutes	None	0.25	0.50
0	1,030,000	1,030,000	1,030,000
10	–	264,000	244,000
20	–	242,000	230,000
30	970,000	192,000	144,000
40	–	147,000	103,000
50	–	–	98,300
60	970,000	113,000	–

Atmospheric oxygen exerts a considerable effect on the length of the stability period. The stability can be lengthened by a factor of about 10 if the Oppanol is processed in an atmosphere of nitrogen instead of air.

Chemical attack at elevated temperature can cause severe molecular breakdown of PIB molecules of any size, while mechanical shear affects only the longest molecules. It seems that PIB, like most other linear polymers, is susceptible to mechanical degradation when molecular weight is well over 1 million. Thermal depolymerization of PIB in solutions apparent from a continuous decline in the viscosity of the solution by prolonged heating.

In addition to depolymerization induced by prolonged exposure to high temperatures, unpigmented PIB is degraded by ultraviolet light. Several specific UV stabilization systems have been developed to minimize this type of polymer breakdown.

Depolymerization can be retarded or prevented by use of stabilizers such as butylated hydroxyl toluene BHT. Commercial grades of Vistanex PIB contain very small quantities of this antioxidant added during manufacture. The amount of BHT added is according to Oppanol type and its molecular weight, as shown in table (2.5) (BASF 2003).

Table (2.5) Stabilizer Content of Oppanol B

Oppanol B	Weight Average Molecular Weight	Stabilizer Content ppm BHT
12 SFN	51000	>1
15 SFN	75000	>1
10 N	36000	100-400
15 N	75000	100-400
30 SF	200000	>1
50	400000	250-500
50 SF	400000	>1
100	1110000	250-500
150	2600000	250-500
200	4100000	250-500
246-250	>5900000	250-500

Oppanol-B 150, 200, and 250 are stabilized also with 2, 6-dilert-butyl-4-methylphenol, which largely prevents degradation of the material during processing. If particularly severe demands are imposed on the stability during processing and on the resistance to ageing. Further stabilization is advisable, e.g., with 0.01 % Iranox 1010 supplied by Geigy Company.

Stabilizers preferably are added to Vistanex polyisobutylene on a mill at about 120°C (250°F). Heat increases the solubility of the stabilizers, though too high a temperature will cause them to volatilize. Heat also reduces the viscosity of the polymer, thus minimizing breakdown by mechanical working. Banbury mixers work the polymer so vigorously that breakdown is accelerated, and they are not recommended for incorporating stabilizers. Another way of adding stabilizers when preparing solutions of PIB is to have the stabilizer in the first increment of solvent added to the PIB.

2.6 Review of Drag Reduction

Drag reduction in fluid flow is an interesting phenomenon and has widely attention from theoretical as well as practical point of view. Therefore the publication on this field is quite large. This section summarized the chief development of the research works on drag reduction.

The drag reduction is well- known phenomenon. This phenomenon was first discovered in 1949 by Toms and has a lot of attention after words because of its practical use in various applications.

Agoston et.al. (1954) covered an essentially unexplored range of flow rates for gasoline thickened with napalm, using standard black pipes ½, 1,and 2 inches in diameter and 21 to 36 feet in length. They brought out a new type of flow anomaly, which become apparent at very high rates of flow, the apparent reduction of viscosity by the addition of thickening agent.

Ousterhout et.al. (1961) conducted experimental work concerning the use of friction-loss reducing additives in fracturing fluids. They used natural and synthetic polymers, soap as drag reducing agents. They found that, if no change in available horsepower is made, the injection rate was increased and an improvement in the over-all fracturing treatment efficiency was obtained.

Savins (1964) added certain types of macromolecules to water and salt solutions flowing in turbulent motion. The result was reduction in the pressure gradients. Alternatively, the volumetric capacity of a pipe of these fluids was increased by the presence of these materials. Savins proposed different several mechanisms to account drag reduction.

Astarita (1965) proposed interpretation of the mechanism of drag reduction in the turbulent flow of viscoelastic liquids, based on the consideration of the frequencies of the non in viscid eddies, which are shown to be higher than the inverse of the relaxation times of those liquids which are usually considered viscoelastic.

Gadd (1965) found that very small traces of certain long- chain molecule contaminants added to water can greatly reduce turbulent friction acting on bodies moving through the fluid, or on surfaces past which the fluid flows. Reductions of as much as 40 percent can be obtained by additions of as little as 10 parts per million by weight.

Union (1966), Friction Reducing Agent (FRA) was developed by Union Carbide's chemicals division. The addition of FRA, which is a water-soluble polymer, to water, had nearly doubled the volume of water flow and the distance of throw.

Hershey and Zakin (1967) concluded that there are two types of drag reduction, each apparently occurring by different mechanisms. In the turbulent region for a given tube, drag reduction occurs above a critical Reynolds number, which is defined as the Reynolds number where the friction factors begin to drop below the values expected for an "ordinary Newtonian" fluid. At Reynolds numbers less than the critical value, the fluid follows the conventional friction factor relationship. They also found that, as concentration of polymer is increased, the critical solution Reynolds number decreases and in same system it eventually becomes less than the laminar-turbulent transition Reynolds number. Drag reduction also occurs in the extended laminar region. In this case the laminar–turbulent transition is delayed to high Reynolds numbers. In their experimental work, they used polyisobutylene (PIB) L-80 in cyclohexane flowing in ½, 1, and 2 inch ID. smooth pipes.

Rodriguez.et.al (1967) obtained correlation between drag reducing characteristics for turbulent flow in a pipe and measurable properties of several polymer solutions. Data obtained in six non polar solvents and literature data for more polar solvents were correlated as the ratio of measured friction factor to purely viscouse friction factor vs. the modified Deborah number ($u\tau_1/D^{0.2}$) where τ_1 is the first- mode relaxation time of the solution.

Hershey.et.al (1967) offered a theory, which permits prediction of the critical Reynolds number in the turbulent flow of polymer solutions. The theory states that the relaxation time of the polymer molecule in solution equals a characteristic flow time for the tube in question at the point of incipient turbulent suppression.

Virk. et.al. (1967) studied experimentally drag reduction caused by dilute, distilled water solutions of five polyethylene oxides, molecular weight from 80,000 to 6,000,000 g/mole, in turbulent pipe flow. Pipes 0.293 and 3.21 cm I.D. were used. They found that the onset of drag reduction occurs at a wall – defined wall shear stress related to the random-coiling effective diameter of the polymer. The maximum drag reduction possible is limited by asymptote that is independent of polymer and pipe diameter.

They stated that three distinct regimes are observed; the laminar region, the turbulent flow region without drag reduction; and the turbulent flow with drag reduction region. They also conclude that the frictional drag reduction, included by a given concentration of polymer, decreases with increasing the pipe diameter.

Wells (1968) presented an analysis, which extends the analogy between energy and momentum transport for turbulent pipe flow for purely viscous fluids to include drag reducing, non-Newtonian fluids. He used the correlation, suggested by Meyer, to predict friction factor and sub layer thickness for the reducing fluids. Analogy made it possible to predict heat transfer rates from simple measurements of pressure drop and flow rate for the drag reducing fluids.

Tanner (1968) exhibited feature of a nonlinear turbulence production term, which was absent from the original Burgers model. Approximate inclusion of triple correlations gave realistic factor-Reynolds number curves.

The viscous term in the model equations was then replaced by a linear viscoelastic term.

Smith (1969) investigated drag reduction in turbulent flow of several polyamide base polymers and was compared with the drag reduction performance of polyethylene oxides. He studied the rheological behavior of these polymers at low concentrations of 100 to 1000 ppm in distilled water, tap water, and synthetic brine containing 8.5 percent NaCl and 2.5 percent $CaCl_2$. He observed that drag reduction increased with molecular weight, concentration, and flow rate for all polymers approaching values of 70 to 80 percent. Smith pointed out that polymer degradation occurs drastically at high flow rates.

Seyer and Metzer (1969) presented an analysis which indicates that laminar annular films of dilute polymeric fluids, used to enable the core fluid or a capsule to slide through a pipeline at reduced pressure drop, are of especial interest in that the normal stress field may generate forces which increase the concentricity of core in presence of major density differences.

Seyer and Metzer (1969) measured the axial and radial turbulence intensities for flow through smooth round tubes in addition to measurements of the time-averaged velocity profiles and the drag coefficients. The results indicated that for solutions exhibiting drag reduction at all Reynolds numbers the flow might be transitional to Reynolds numbers of the order of 10^5.

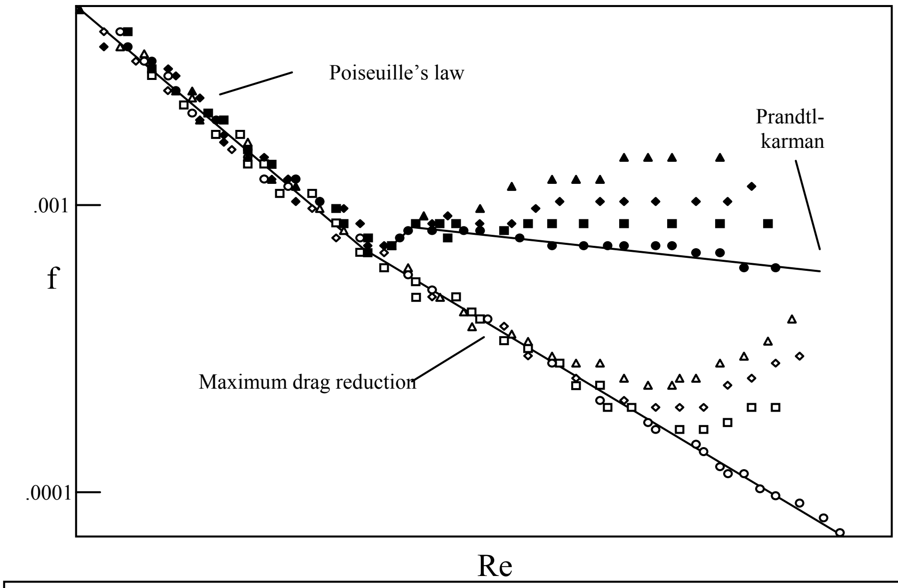


Fig. (2.5) Friction factor plot for maximum asymptotic drag reduction in rough pipes. Solid points refer to solvent. Hollow points to polymer solutions yielding maximum drag reduction

Symbol	Roughness (R/k)
△ ▲	14.6
◇ ◆	22.8
□ ■	55
○ ●	Smooth

Virk[I] (1971) conducted experimental work concerning the drag reduction caused by dilute, distilled water solution of four polyethylene oxides and one polyacrylamide, of high molecular weights of $0.1*10^6$ to $8*10^6$ and $13*10^6$, respectively. One smooth and three sand-roughened pipes were used to induce maximum possible drag reduction in each pipe and the onset of roughness as shown in figure (2.5). Then he obtained the maximum viscous sub layer thickness during the drag reduction.

Virk[II] (1971) presented an evidence of a universal maximum drag reduction asymptote. He stated that; in a general case of drag reduction, the mean velocity profile consists of three segments, a viscose sub layer, elastic sub layer and newtonian plug.

Lescarboura et al (1971) investigated polymeric drag reducer in an 8 inch diameter crude oil pipeline. The test segment was 28 miles long. At the normal flow velocity in the 8 inch line of about 6 ft/sec, Drag reduction of 16, 21 and 25 percent where obtained at polymer concentrations of 300, 600 and 1000 ppm. They found that drag reduction decreased with the velocity. They presented an equation that correlates the 8 inch and 12 inch data as a function of flow velocity and polymer concentration.

Sarem (1973) revealed that drag reduction is not a continuously increasing function of the flow velocity. He showed that the drag reduction increases as velocity increases up to “a critical” velocity of a 9.8 ft/sec. As the velocity is increased beyond 9.8 ft/sec the drag reduction gradually decreases.

Lee.et.al (1974) showed that polymeric solutions and fiber suspensions exhibit different mechanisms of drag reduction. They obtained drag reduction excess of 95% in 3.4 cm tube at Reynolds number 100,000.

Virk et.al (1975) reviewed drag reduction by dilute solutions of linear, random-coiling–macro-molecular in turbulent pipe flow. Their review was intended to convey some of the experimental facts and theoretical understanding of drag reduction. Their experimental information was summarized by empirical correlations based on the elastic sub-layer model of drag reduction.

Gustavsson (1977) conducted drag reduction experiments using polystyrene in toluene. He used polymer sample with a molecular weight 2,000,000 at different concentration. He found the thickness of this layer is proportional to the concentration to the power 0.75.

Savins and Seyer (1977) presented a drag reduction correlation based on friction velocity and the availability of some turbulent flow data for six pipe diameters: 4.09, 5.05, 6.2, 10.2, 12.6 and 16.2 cm.

Stenberg.et.al (1977) state that turbulent drag reduction induced by injection polymer into pipe flow exhibits major changes with variation of the rotational speed of an upstream mixer. This was shown unify the concepts of homogeneous and heterogeneous drag reduction.

Burger.et.al (1980) conducted experiments in the TAPS pipeline (Trans Alaska Pipeline System) using drag reducing additives. They concluded that drag reduction was increased with increasing velocity, decreasing diameter, and decreasing viscosity.

Sifferman. et.al (1981) observed drag reduction three distinctly different flow systems –dilute polymer solution, two phase solid/liquid suspensions, and three-phase immiscible liquid/liquid flow with suspended solids-in relatively large-diameter pipes (0.027, 0.038 and 0.053 m).They observed that drag reduction of up to almost 80% for both the polymer systems, and the oil system. They obtained sand suspensions had a maximum of about 35% drag reduction in tap water. Greatest reductions (more than 90%) were attained with the polymer/suspensions.

Berretz et.al (1982) stated that maximum performance can be realized when the hydrocarbon is a light crude oil or a refined product such as gasoline. They conducted experimentally that lighter crude oil has higher percent drag reduction than heavier crude oil flow at same drag reducer concentration as shown in figure (2.6).

Beaty et.al (1982) developed new high performance flow improver, which called CDR $_{102}$ .They found CDR $_{102}$ flow improver was three to five times more effective than the standard CDR$_{101}$ material as given in figure (2.7).

Darby and Chang. (1982) developed a correlation based upon the concept of energy dissipation in viscoelastic fluid, which enables the prediction of friction loss of "concentrated" fresh and shear degraded polymer solutions of several concentrations in a wide range of tube sizes. The correlation involves a generalized definition of the fanning friction factor ($f_p=f_s/(\sqrt{}1+NDe^2)$) which accounts for the effect of viscoelastic properties on friction loss, and enables friction factor data for drag reducing fluids to be represented by the same classical correlation that represent ordinary Newtonian fluids.

Motire (1985) used the commercial DRA. The available DRA was dissolved in highly aliphatic solvents. This property allows for the maximum, efficiently found in highly aliphatic, low viscosity fluids, such as gasoline and fuel oil. Kirkuk crude oil, using DRA, gave increasing the flow rate from approximately (1,230) bbl/hr to (1,300) bbl/hr.

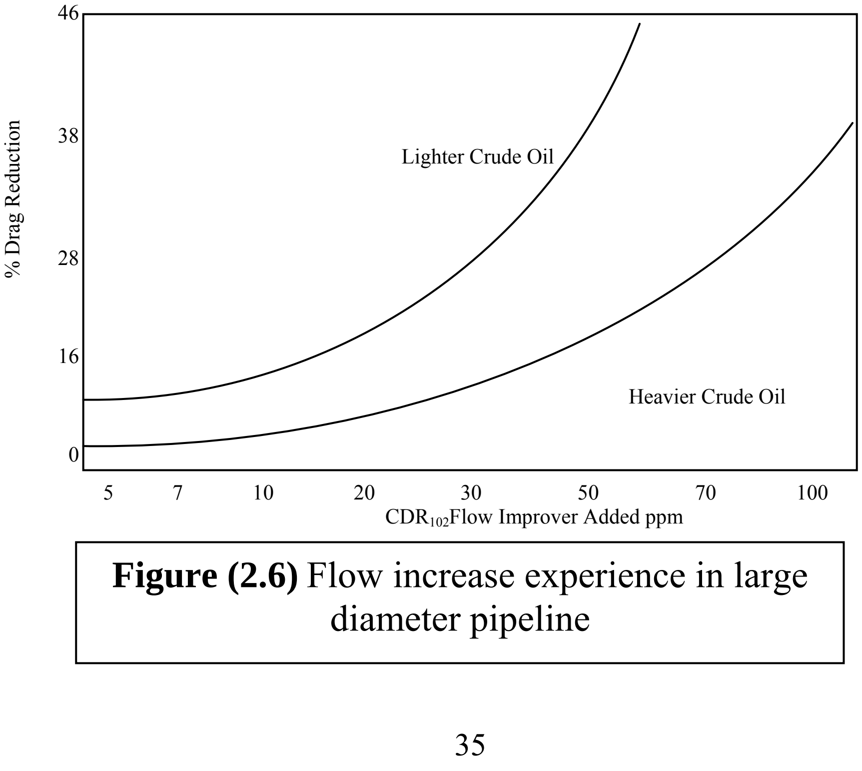


Figure (2.6) Flow increase experience in large diameter pipeline

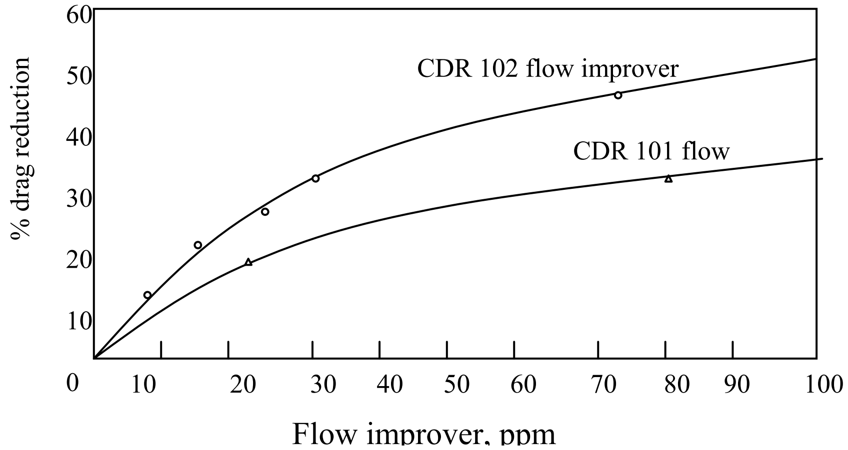


Figure (2.7) Performance in 1inch flow loop

Lester (1985) summarized the factors that affected the DRA performance. He stated that the effectiveness of a DRA depends to a certain extent on the viscosity of the untreated oil and decreases as viscosity increases. Also the effectiveness of DRA varies slightly with diameter and decreases as diameter increases.

Horn et. al (1986) showed that drag reduction was indeed possible in fluids of high viscosity. The results also proved that a high Reynolds number is not a requirement for effective drag reduction, which can occur in flow systems that are in fact only partly turbulent.

Mansour and Aldoss (1988) carried out number of experiments to investigate the effect of soapy industrial cleaner on reducing the skin friction of crude oil flowing turbulently in pilot-scale pipes of different sizes. Experiments showed that a concentration of only 2 ppm of a chemical additive injected into crud oil line caused an appreciable amount of drag reduction in different pipes was achieved.

Mansour and Aswad (1989) tested experimentally a new drag reducing chemical additive (GEM) to minimize skin friction in turbulent pipe flow of Iraqi crude oil using large-scale pipes of 1, 2, 3, and 4 inch size. A friction reduction up to 63% has been achieved when 9 ppm of additives was added to crude oil. The effects of flow rate, pipe diameter, and additive concentration on the rate of drag reduction have been experimentally tested.

Keck (1991) introduced numerically generalized velocity profiles for the near wall region of turbulent pipe flow. These profiles were integrated to generate friction factor versus Reynolds number expressions with Deborah number as a parameter.

Berge and Solsvik (1996) conducted different tests using both conventional gel-type DRA, and a new generation type additive. The new generation DRA was an emulsified powder product with a polymer content of about 20-25%. This new type turns out to be about four times efficient, in reducing drag, than conventional gel- type, DRA. They also measured the drag efficiency as a function line fill and showed the relationship between injection rate of DRA and wax- deposits in a pipeline.

Warhholic et.al (1999) used a two–component laser- doppler velocimeter, with high temporal resolution to study how the introduction of a drag –reducing surfactant to water changes the fully – developed velocity field in an enclosed rectangular channel. They concluded that solutions of surfactants in water could be formulated so that rod- shaped micelles are created. The presence of these micelles causes a long reduction in drag over what would be experienced with a Newtonian fluid flowing turbulently at the same rate.

Lin.et.al (2000) investigated one –to-one molar ratio sodium salicylate (5mM)/ Arqui 5-50 (5 mM) solution, in comparison to sodium salicylate (12.5 mM)/ Arqui 5-50 (5 mM) or 2.5: 1 solution. Results showed a dramatic influence of the counter ion to the surfactant concentration ratio on the viscoelasticity of the surfactant drag reducing systems. The 1:1 solution has normal surfactant drag reducer characteristics such as viscoelastic properties and thread- like micellar networks and branches.

Beris (2000) developed of a theoretical quantitative understanding of the dynamic of high Reynolds number free surface flows under large free surface deformations in the presence of one or multiple surfactants on turbulence, waves, slick formation, and mass transfer through the free surface.

Lin et. al (2000) reported experimental studies of the effects of mixtures of cationic surfactants on their drag reduction and Rheological behaviors. Cationic alkyl- trimethyl quaternary ammonium surfactant with alkyl chain lengths of C_{12} and C_{22} were mixed at different molar ratios. (Total surfactant concentrations were kept at 5 mM with 12.5 mM sodium salicylate as counter ion. Drag reduction tests showed that by adding 10% mol of C_{12}, the effective drag reduction range expanded to (40-120) °C compared with 80-130 º C with only the C_{22} surfactant.

Nishimura et.al (2001) conducted experiments to examine the near field characteristics of the ax-symmetric jet discharged from along circular pipe for a dilute surfactant solution (Ethoquad O/12). The solvent Reynolds number covers from 5000 to 20000 in which, drag reduction occurs in a circular pipe of 10 mm in diameter. They showed that for this Reynolds number range, a remarkable change in the radial spreading width is observed, unlike the case of pure water.

Lin et.al (2001) compared the effect of concentration of the counter ion and its ratio to surfactant concentration on drag reduction, Rheological behavior, and microstructures. They found Arquad 16-50 (commercial CTAC, cetyltrimethylammonium chloride) (5mM) with the counter-ion 3, 4-dichlorobenzcate (5 and 10 mM), 3, 4-dimethylbenzcate (5 and 10 mM) solutions are good drag reducers at different temperature ranges.

Myska and et.al (2001) studied the properties of many cationic and zwitter ionic surfactants. The hydrodynamic radius of the micelles, the shear and a extensional viscosity of the solutions at concentrations appropriate for drag reduction were investigated. They concluded that zwitter ionic surfactant and a mixture of cationic CTAC with Na-Salicylate are excellent drag reducers with the ability to decrease friction losses by more than 90%.

Lin et.al (2001) studied rheological behaviors and microstructure of cationic surfactant Ethoquad O/12 at concentration range from 5 mM to 200 mM with counter ion sodium salicylate to surfactant molar ratio of 1 and 2.5. They found that the shear viscosity has shown complicated trends. For the first series, 5 mM/5 mM and 10 mM /10mM solutions were highly shear thinning, while surfactant concentrations highly than 50 mM showed Newtonian behavior up to a shear rate a round 10, followed by some shear thinning. On the other hand, shear viscosity did not show any dramatic changes with shear rate for the ratio of 2.5 solutions.

Sung et. al (2003) investigated the cationic surfactant system as high resistance materials to turbulent flow.

Ptasinski et. al. (2003) state that at higher drag reductions, larger than about 40%, the flow enters the high drag reduction regime for which the slope of the log-law is dramatically augmented and Reynolds shear stress is small.

Chapter Three

Experimental Work

3.1 Materials

The hydrocarbon soluble, polyisobutylenes, grade Oppanol 150, 200, and 250 with three different molecular weights of $2.6*10^6$, $4.1*10^6$ and $5.9*10^6$ g/mole were acquired from BASF Company, Germany. The water soluble carboxymethylcellouse (CMC) of a molecular weight, about $0.4*10^6$ g/mole, was supplied by the General Company of Vegetable Oil Industries, Baghdad. Five hydrocarbon-nature solvents were chosen to provide diverse aromatics content and boiling range. Light naphtha, heavy naphtha, xylene, reformate and special spirit (SS1) were supplied from Al-Durra Refinery. The main properties of oil –solvents are listed in table (3.1) while De-ionized water was used for dissolving CMC .

Table (3.1) Properties of Oil Solvents

Solvents	Boiling Range ºC	Specific Gravity at 15.6 ºC	Approximate aromatics Content vol.%
Light naphtha	34-85	0.6590	1
Heavy naphtha	100-150	0.7412	5
Reformate	80-200	0.7634	50
Special spirit (SS1)	70-120	0.705	10
Xylene mixture	136-145	0.8710	99

Gas oil of 260 ºC initial boiling point, 360 ºC end-point and about 39 API gravity at 15.6 ºC was brought from Al-Durra Refinery as stock-tank fraction. It was used in addition to tap water in drag reduction measurements.

3.2 Preparation of Polymeric Solutions

The dissolving of high molecular weight polymers were carried out in a shaking machine, type KOTTERMANN 4010, GERMANY, 100 rpm at room temperature (25-30)°C very carefully as shown in figure (3.1). This condition was used to avoid any polymer molecular degradation since the stirring device has no blade or sharp edge that could expose the polymer to high shear force.

The method of solution preparation adapted here was to make 2 % by weight concentration in a separate container. Thus, 5 grams of corresponding Oppanol type was placed in a one liter conical flask and mixed with 250 gram of the corresponding solvent. The container was placed in the electrical shaker, the shaker was started at 40 rpm and increased by 10 rpm after every 24 hours, and a homogenous solution was obtained after 2 days for Oppanol B 150, 3 days for Oppanol 200 and 5 days for Oppanol B 250. The solution was allowed to stand at least 24 hours at room temperature prior to further investigations. 10 gram CMC in 250 gram de-ionized water was used to prepare 4 wt.% CMC solution by using the same procedure as mentioned above.

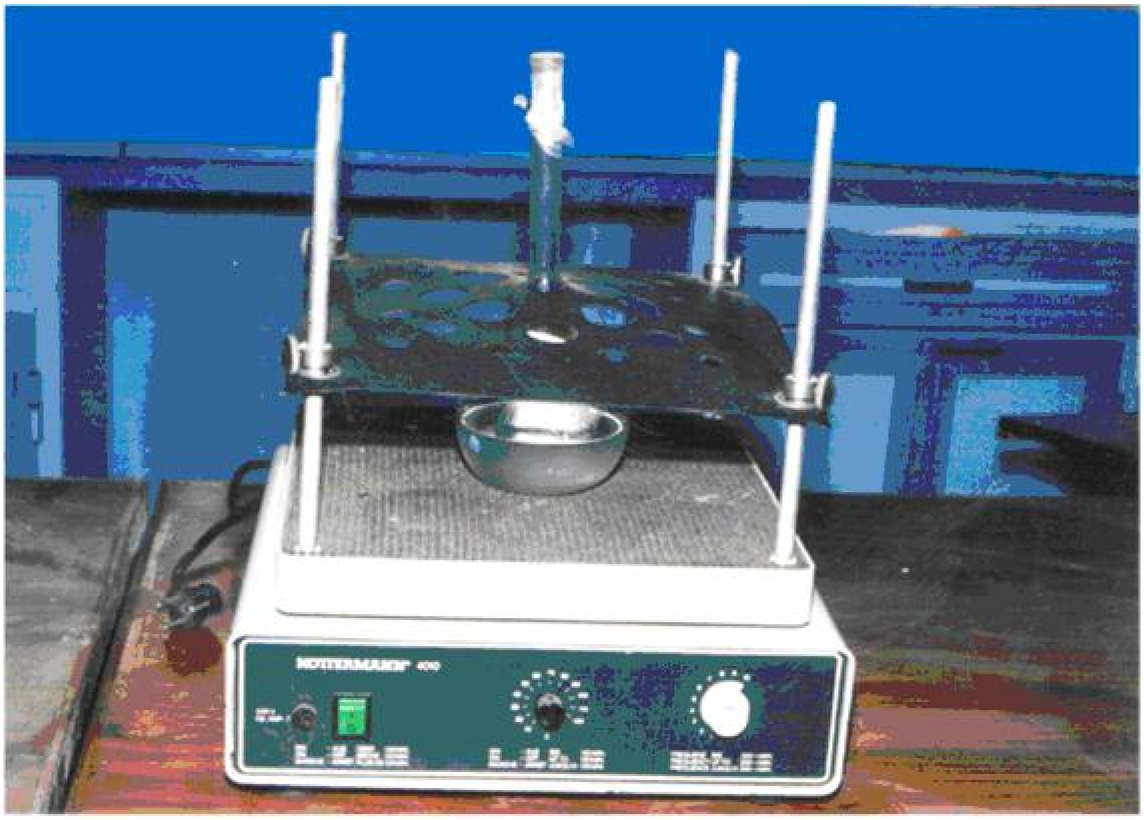


Fig. (3.1) Shaker machine

3.3 Density and Viscosity Measurements

Density and viscosity of polymeric solutions were determined at different concentrations and temperatures up to 45ºC. The density determination were carried out using pyknometer size 50 cm^3 according to the standard method (IP 190) (API 1988).The calibration of the pyknometer was done by determination the density of distillate water. The samples weights were measured by a sensitive digital balance type (SARTORIUS, BL15005 AG GOTTINGEN, GERMANY) to range 0.01 mg.

The pyknometer was placed in a water bath type (MEMERT GMBH+CO. KG D-91126 SCHWABACH FRG WB 10, GERMANY) which was capable of maintaining temperature within ±0.1ºC of the selected temperature, to make the sample get the test temperature. Thoroughly clean the pyknometer and stopper with a cleaning fluid (light naphtha, chromic acid), rinse well with distilled water, then with acetone and dry. Ensure that all traces of moisture are removed by drying with a current hot air passing through the pyknometer and stopper capillary. Wipe the outside of pyknometer and stopper with a clean, lint-free cloth. Normally pyknometer cleaned by washing with a suitable light petroleum solvent (light naphtha), followed by drying. All the density measurements are carried out at atmospheric pressure.

Viscosity measurements at different temperatures were performed by using different sizes of BS/U tube viscometer as shown in figure (3.2) which are satisfy kinematic viscosity range (0.9-10000 mm^2/s) according to the standard method (IP.71) as shown in table (3.3).

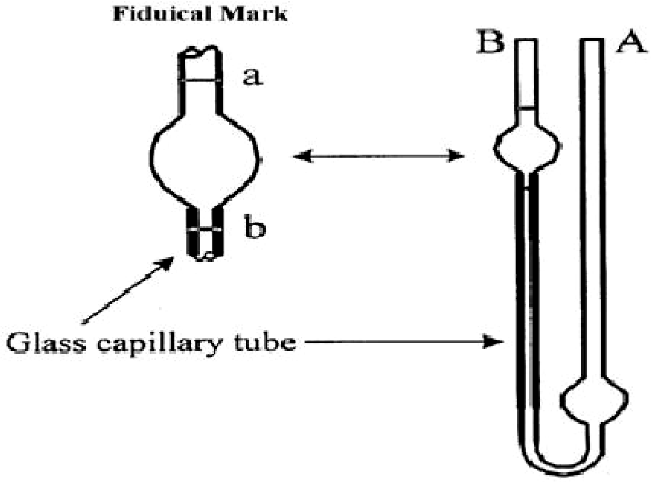


Fig. (3.2) BS/U Tube Viscometer

Using of BS/U tube viscometer, to ensure more accurate viscosity measurements because this type has two bulbs which enable the fluid to reach steady state condition.

Table (3.2) Kinematic Viscosity Range

Size No.	Nominal Viscometer Constant B (mm^2/s)/s	Kinamatic Viscosity range (mm^2/s)
A	0.003	0.9 to 3
B	0.01	2.0 to 10
C	0.03	6 to 30
D	0.1	20 to 100
E	0.3	60 to 300
F	1.0	200 to 1000
G	3.0	600 to 3000
H	10.0	2000 to 10000

The viscometer was placed in water bath which was capable of maintaining the temperature within ± 0.1ºC of the selected temperature. Measurement of the kinamatic viscosity was determined by the standard method of test and international standard ISO 3105, with accuracy ±0.006 cp. The viscometers were calibrated with pure hydrocarbon of known viscosity. A stop watch was used to measure the time.

The kinematic viscosity, *v*, was calculated from the measured flow time, t, and the viscometer calibration constant by using:

$$\nu = \beta * t \qquad \ldots(3.1)$$

Where *v* is the viscosity in centistock, β is the viscometer constant centistock / second and *t* is the flow time in second.

Duplicate measurements did not deviate more than 0.36% about their mean. Repeatability measurement should not deviate more than 0.7% about their mean. The dynamic viscosity can be determined by using the following equation:

$$\eta = \frac{\nu}{\rho} \qquad \ldots(3.2)$$

Where ρ is the density in kg/m^3.

3.4 Drag Reduction Measurements

3.4.1 Flow loop

The performance of the drag reducing additives was evaluated in a laboratory scale circulation loop (Niazzi 2006). The schematic diagram of the experimental set up is shown in figure (3.3).

The fluid container of about one m^3 capacity was fitted with a positive displacement gear pump of 50.8 mm diameter and 1440 rpm. This type of pump was used to avoid polymer mechanical degradation, which reduced usually the drag- reducing efficiency. Carbon steel pipe of 0.03175 m inside diameter was used to perform the flow measurements. The test section is 2 m long and located away from the entrance to get fully developed region. The minimum entrance length, Le was about (1.6 m) and was calculated by the relationship suggested by Desissler (Desissler 1950), as follows

$$Le = 50 \times D \qquad \ldots(3.3)$$

The fluid flow was controlled by means of ball valves; the pressure drop in test section was measured by U- tube manometer filled with mercury and an invert manometer.

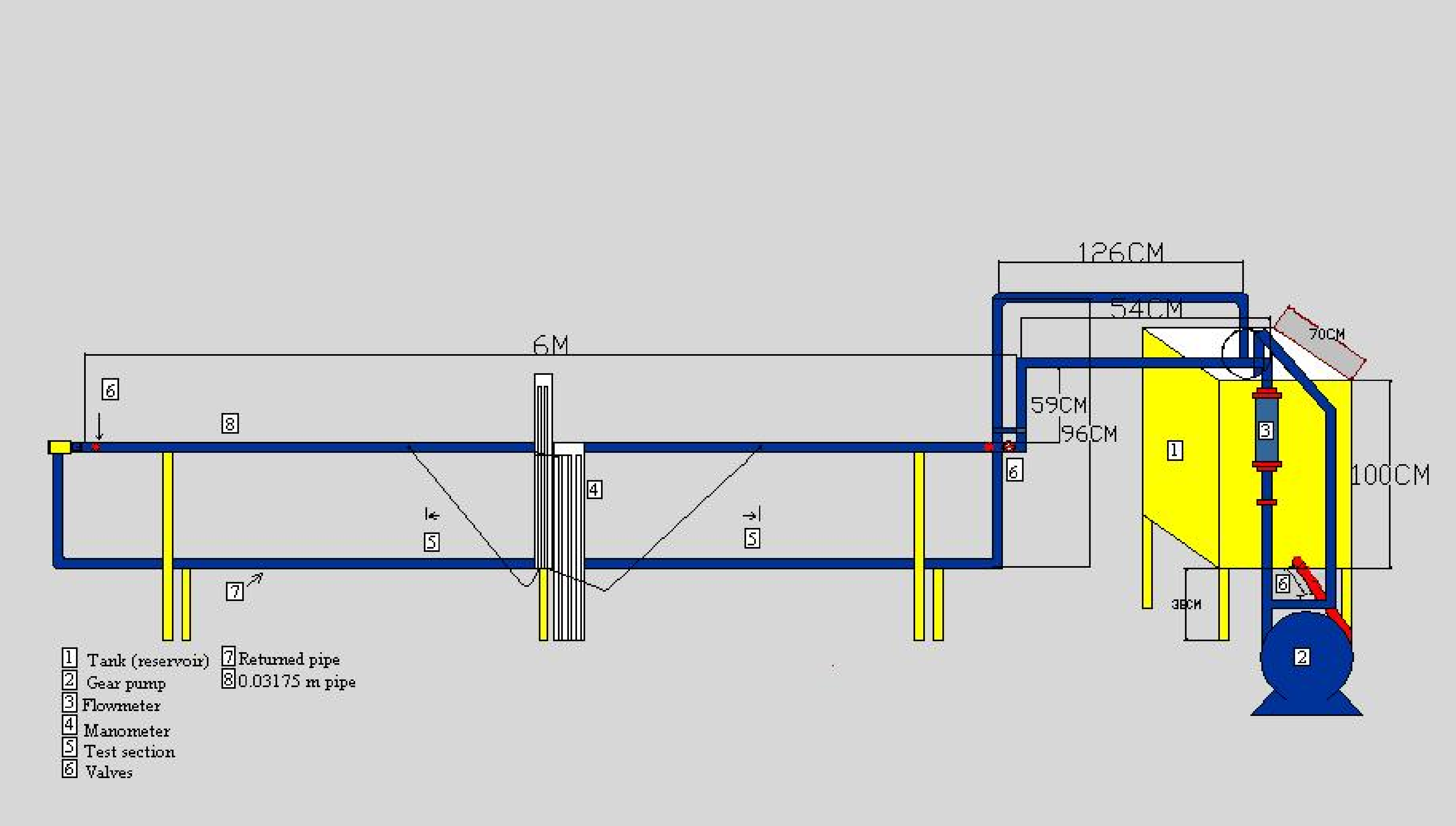


Fig. (3.3) Schematic diagram for the rig

The gas oil or water flow rates were measured with a float flow meter, of 50.8 mm diameter and flow indicating range between 10-100 lit./min.. Figure (3.4) shows the calibration of flow meter.

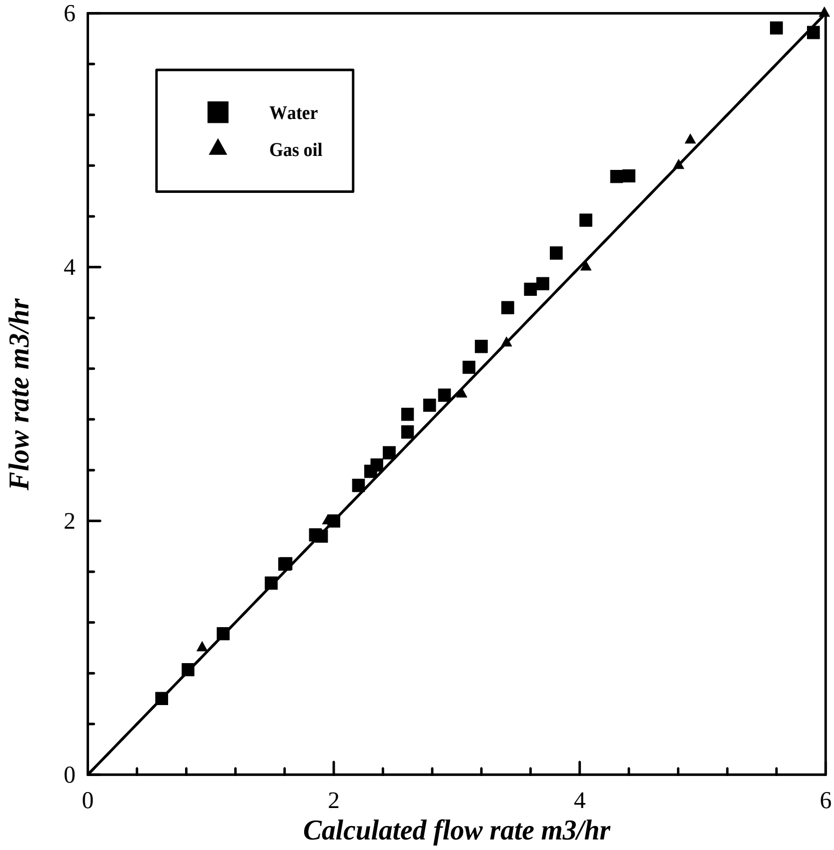


Fig. (3.4) Calibration of flow meter

3.4.2 Experimental Procedure

The drag- reducing effect of additives under turbulent flow conditions were evaluated by measuring the pressure drop- flow rate relationship when the test fluid was forced to flow in the circular flow system.

The container was filled initially with 130 liters of corresponding fluid, gas oil or water. The fluid was allowed to flow through the pipe by operating the gear pump. The flow rate was maintained constant by means the corresponding valves. The experiment was stopped after obtaining a stabilized pressure drop reading.

The same procedure was done to measure the pressure drop-flow rate for treated gas oil or water. In order to insure a homogenous mixture, it was decided to dilute the drag- reduction additives prior to add to the feed tank. The appropriate amount of concentrated additive solution was diluted by about half liter of test fluid, and stirred slowly for about one hour by a shaker, and left 24 hour at laboratory temperature. The prepared solution was added carefully into the feed tank. Typically about 20 minutes of mixing by operating the pump were allowed prior to performing the test. Figure (3.5) show the experimental set-up.

Fig. (3.5) Experimental set-up

Chapter Four

Results and Discussion

4.1 Dissolving

Hydrocarbon soluble Oppanol B type polyisobutylene with three molecular weights were chosen to prepare stable solutions for drag-reducing purposes. The polymers have a molecular weight of $2.6*10^6$, $4.1*10^6$ and $5.9*10^6$ g/mole and are considered to be flexible and linear. Such polymers undergo undesirable mechanical and chemical degradation due to shear stresses, elevated temperature and energetic radiation effects (Rho. 1996). Therefore care should be taken during their dissolving and transfer.

More details of the dissolving procedure are given in part (3.2) of chapter three of present thesis. The main observation, which was noticed during the dissolving experiments are summarized as follows:

1. The rate at which Oppanol B drag reducers are dissolved or swollen by homologous solvents is inversely proportional to the solvents molecular weight. Therefore the rate of dissolving in light naphtha > in heavy naphtha > in special spirit. Furthermore the aromatic of the solvent enhances its solubility effect. Xylenes and reformate exhibited promising capabilities in dissolving the polymers.

   Reformate of about 50% aromatic content and of (80-200) ºC boiling range is shown to be the best solvent for all studied Oppanol B types. Furthermore it can be considered as economical solvent compared with individual aromatics, such as benzene or toluene.

2. The dependence of the dissolving of Oppanol B polymers is a function of molecular weight. Rate of dissolving Oppanol 150 (Mw $2.6*10^6$g/mole) > Oppanol B 200 (Mw=$4.1*10^6$ g/mole) > Oppanol B 250 (Mw=$5.9*10^6$ g/mole).
3. The dissolving process undergoes two main stages. Firstly, the polymer is a swollen producing swollen gel followed by a diffusion and dissolving stage forming colored solution, beginning from yellow to light brown during the dissolving time. During the dissolving process, the solution become more viscous resulting in difficulties in the mixing. Therefore it was not easy to get higher polymeric concentrations.
4. The required time to get 2 wt. % homogenous polymeric solutions was two days for Oppanol B 150, three days for Oppanol B 200 and five days for Oppanol B 250.

Carboxymethylcellulose, CMC as a polar compound can be dissolved in water. The dissolving process is similar to that for Oppanol B polymers, as described previously. CMC was swollen and dissolved, due to its polarity and low molecular weight of about $0.4*10^6$ g/mole, which is faster compared to Oppanol B polymers of high molecular weights ranging between $2.6*10^6$ to $5.9*10^6$ g/mole. Therefore a 4 wt. % homogenous CMC solution was obtained in one day shaking. At higher concentrations, the solution became dull and more viscous. 4 wt. % solution is considered as the maximum under the described conditions.

4.2 Viscosity of Polymeric Solutions

4.2.1 Effect of Concentration

The viscosity of high molecular weight polyisobutylene in reformate solvent differs decidedly owing to the differences in the degree of solubility. This is illustrated in figures (4.1) and (4.2), in which the viscosity of various Oppanol B, 150, 200 and 250 concentrations at 298 and 318 K. While the relationship between viscosity and concentration for solutions of CMC in water is shown in figure (4.3).

Figures (4.1) through (4.3) show that the viscosity of polymeric solutions increases dramatically with the increase in concentration, a gradual increase of viscosity was observed at concentration above about one wt. %. Thus the solutions at such elevated concentrations become more viscous and difficult to mix or to handle.

Furthermore, figures (4.1) and (4.2) indicate, that the viscosity of Oppanol solutions is a function of molecular weight of the dissolved polymer. Therefore the values of viscosity are in the order Oppanol B 150 < 200 < 250 for the same concentrations. This lead to the fact, that the maximum concentrations to measure the viscosity for the above mentioned polymers were 1.5, 2 and 2 wt. % respectively. Above these concentrations the viscosity experiment becomes difficult at temperatures (298-318) K in BS/U tube viscometers.

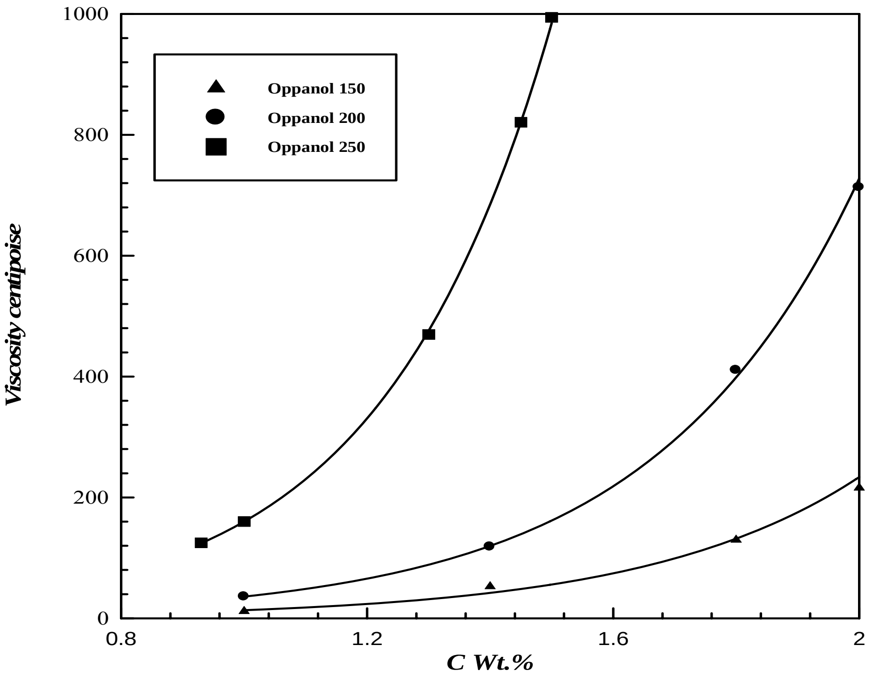


Fig. (4.1) Effect of concentration on viscosity of Oppanol B solutions at 298 K

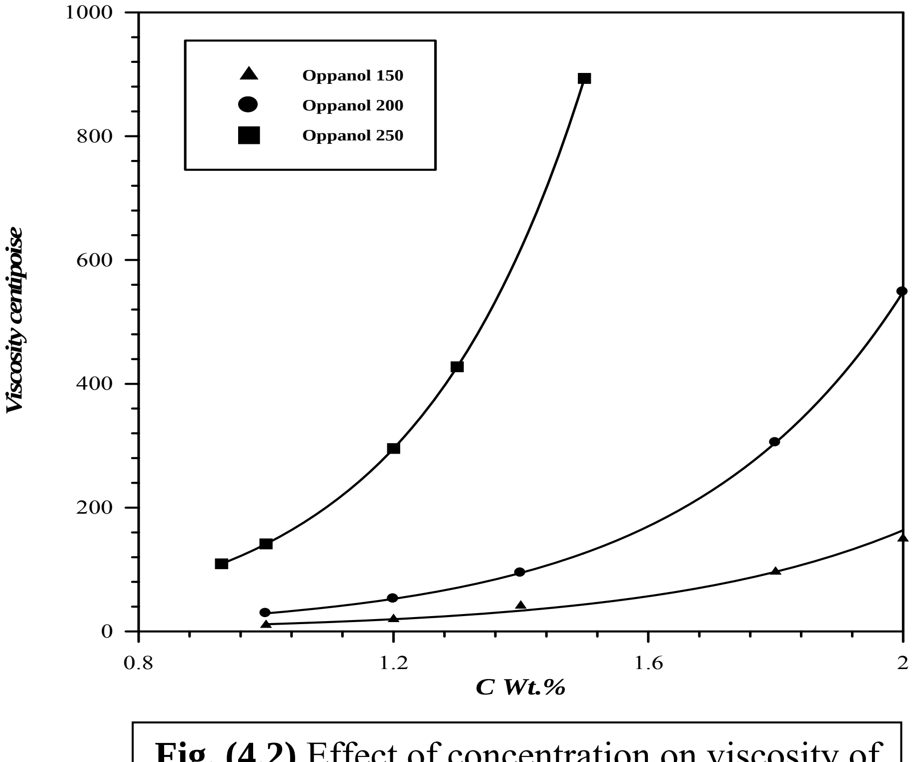


Fig. (4.2) Effect of concentration on viscosity of Oppanol B solutions at 318 K

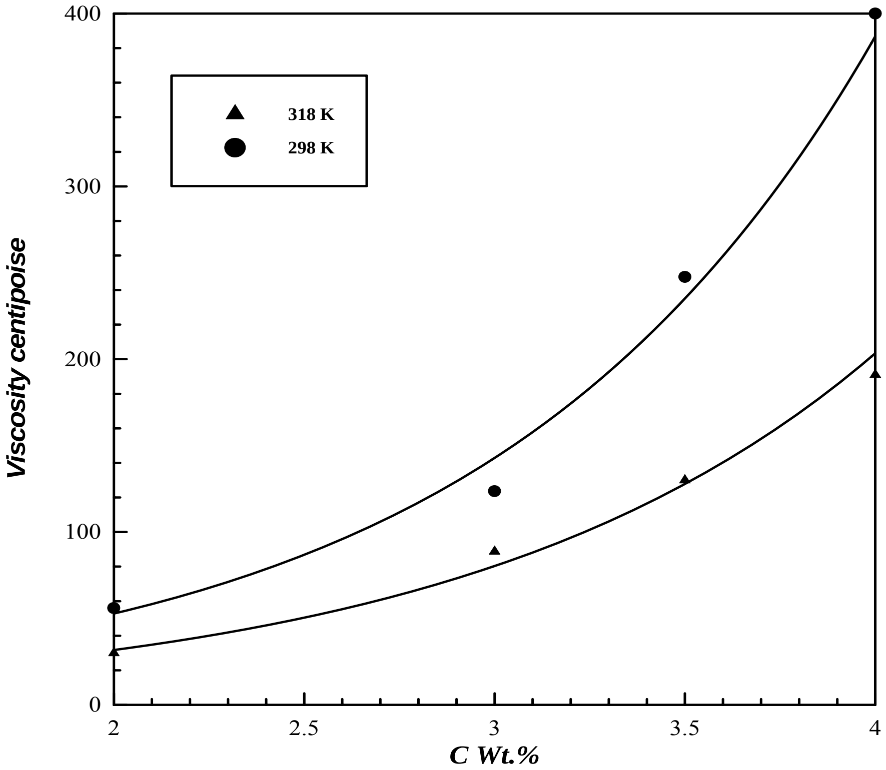


Fig. (4.3) Effect of concentration on viscosity of CMC solutions at 298 and 318 K

Figure (4.3) shows, the viscosity for CMC in water increases directly for concentrations above 2 wt. %. Generally, solutions of CMC exhibit lower viscosities compared to those for Oppanol B type polymers at similar concentrations. This is due to the fact that CMC has a relatively low molecular weight $0.4*10^6$ g/mole compared to Oppanol B types of molecular weight ranging ($2.6*10^6$ - $5.9*10^6$ g/mole). Therefore the viscosity of CMC in water was easy to measure for concentrations up to about 4 wt. %.

4.2.2 Temperature Dependence

The relationship between the viscosity of polymeric solutions and temperature is illustrated in figures (4.4), (4.5) and (4.6) for Oppanol B polymers and in figure (4.7) for CMC solutions. These figures shows the lowering of viscosity with temperature increase in the range (298-318) K. Higher temperatures were not considered in present investigation, due to the sensitivity of such drag-reducing polymers to elevated temperature, and undergo possible molecular degradation (Rho 1996).

The sensitivity of viscosity with temperature variations depends on the value of viscosity. Thus the high viscous solutions, as in case of Oppanol B 250 was affected more by temperature increase.

The viscosity of 4 wt. % CMC in water undergo significant reduction by temperature increase, as shown in figure (4.7). It dropped from 400 centipoise at 298 K to about 191.7 centipoise at 318 K.

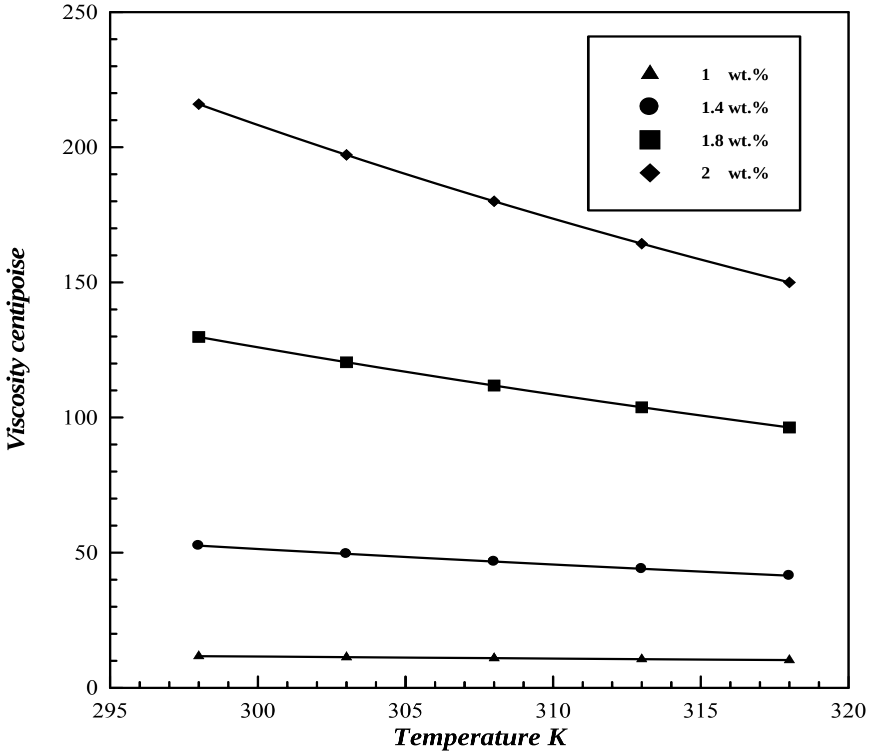


Fig. (4.4) Temperature versus viscosity for Oppanol 150 solutions

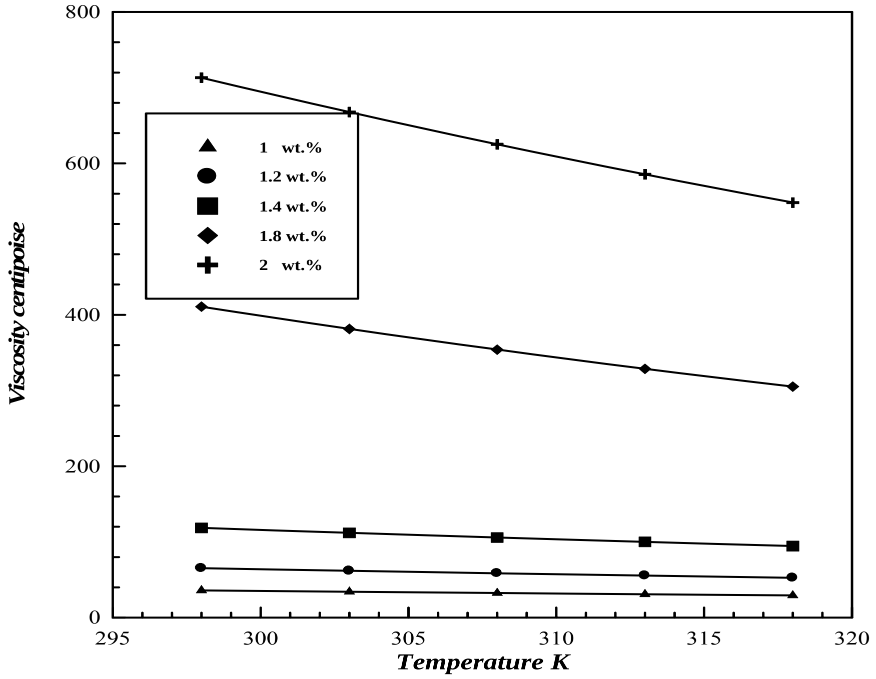


Fig. (4.5) Temperature versus viscosity for Oppanol 200 solutions

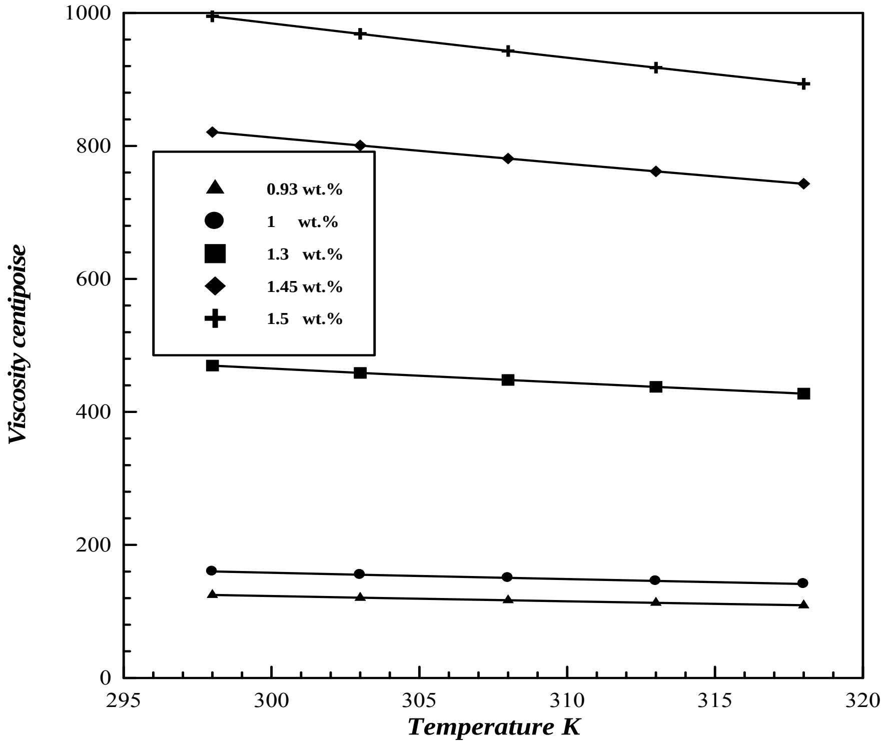


Fig. (4.6) Temperature versus viscosity for Oppanol 250 solutions

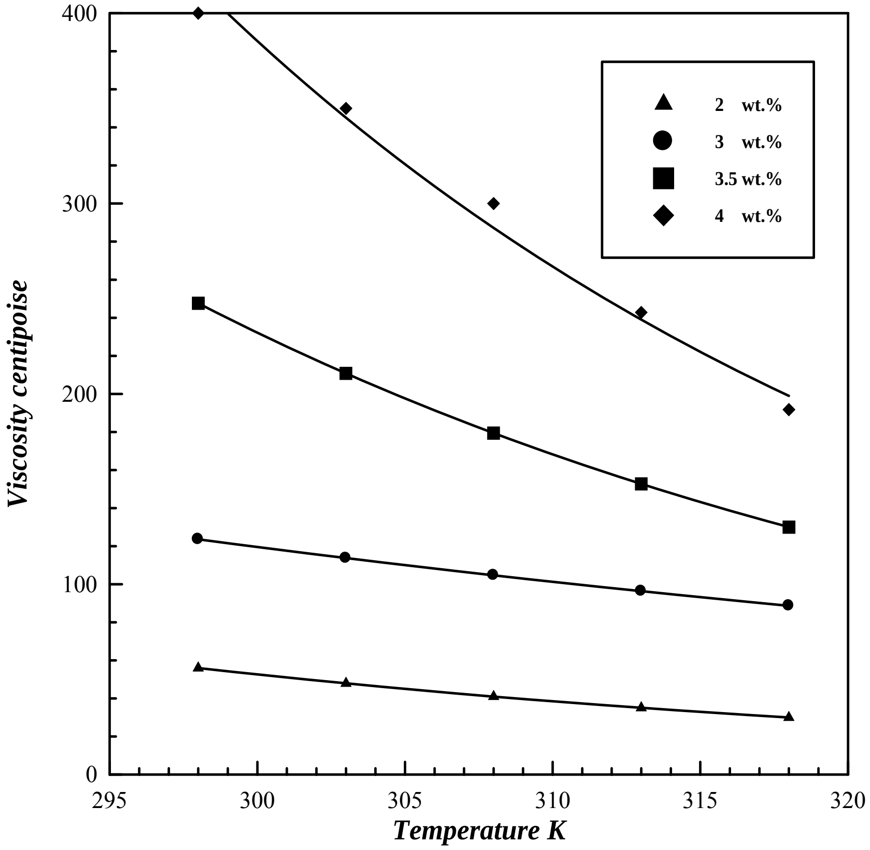


Fig. (4.7) Temperature versus viscosity for CMC solutions

4.3 Density of Polymeric Solutions

4.3.1 Concentration Dependence

The densities of Oppanol B, 150, 200, and 250 in reformate are illustrated in figures (4.8) and (4.9) as a function of concentration at temperature 308 K and 318 K respectively. While the concentration dependence of density for CMC in water is shown in figure (4.10) for the two temperatures.

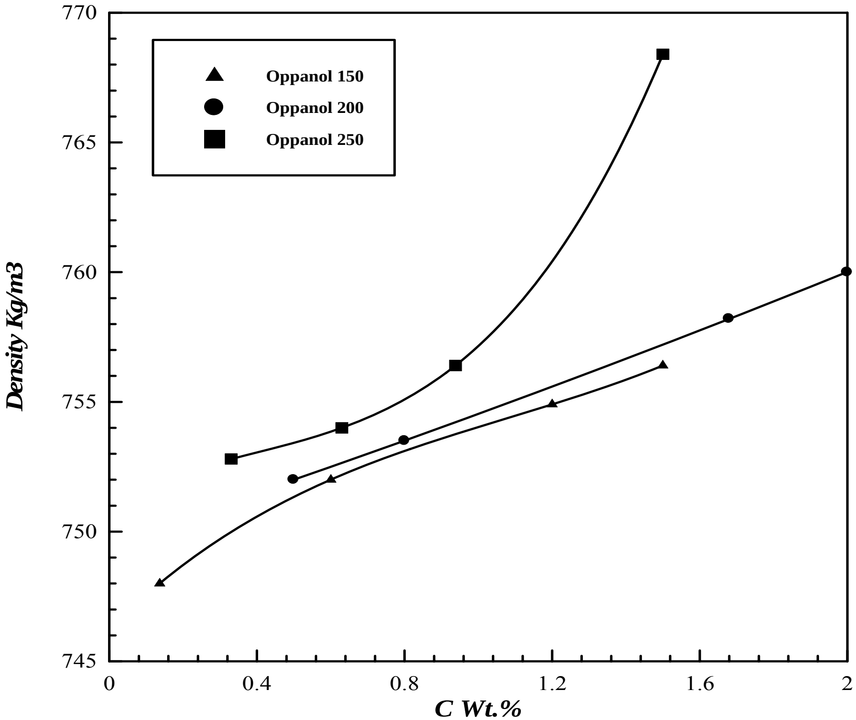


Fig. (4.8) Effect of concentration on density of Oppanol B solutions at 308 K

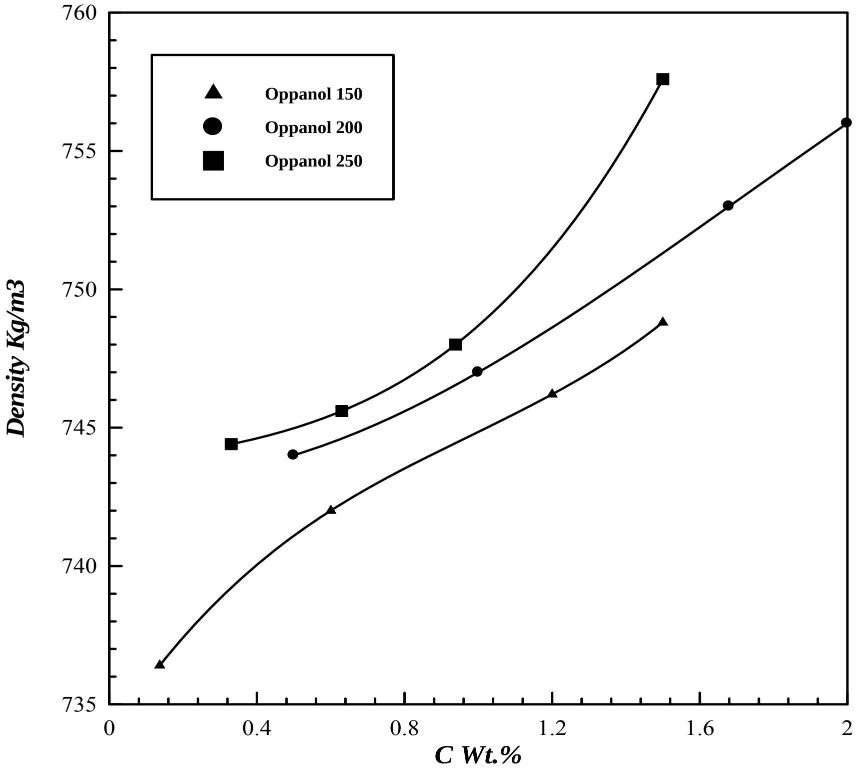


Fig. (4.9) Effect of concentration on density of Oppanol B solutions at 318 K

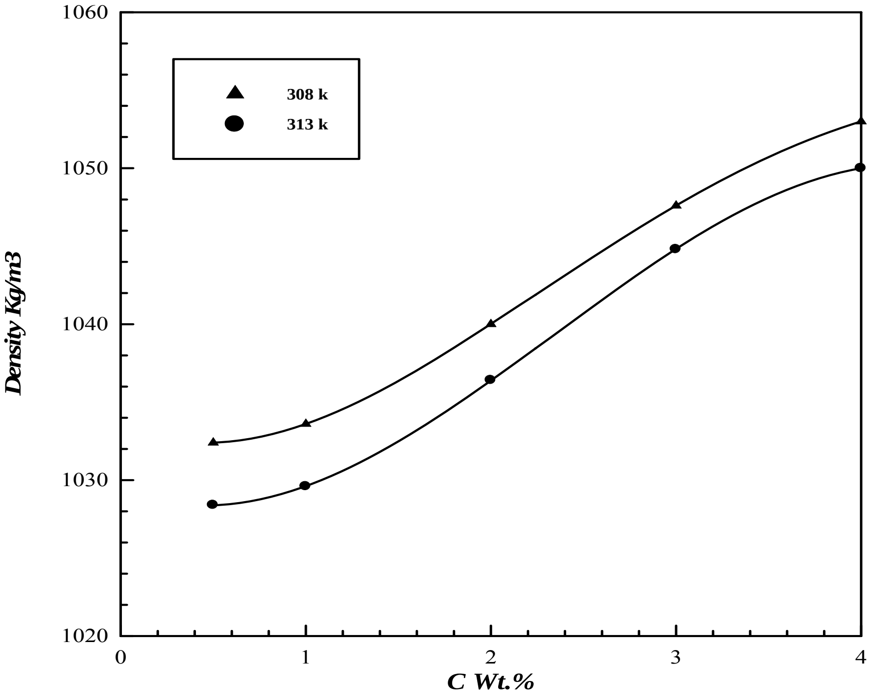


Fig. (4.10) Effect of concentration on density of CMC solutions at 308 and 313 K

The results show clearly, that the density of Oppanol solutions increases with the increase in molecular weight of the polymer and with its concentration. Table (4.1) gives the density values for the Oppanol B types and CMC solutions at two different concentrations to compare the concentration and the molecular weight dependence of density.

Table (4.1) Densities of Polymeric Solutions At Two Different Concentrations

Polymer Type	Molecular Weight (g/mole)	Density (Kg/m^3)	
		0.5 wt.%	1.5 wt.%
Oppanol B 150	$2.6*10^6$	750	756.4
Oppanol B 200	$4.1*10^6$	752	758.2
Oppanol B 250	$5.9*10^6$	753.5	768.4
CMC	$0.4*10^6$	1032.4	1036.4

It is worth mentioning, that the density of CMC solutions is always greater than thus of Oppanol solutions, due to the polarity of CMC and water is denser than reformate solvent.

4.3.2 Temperature Dependence

The variation in density with temperature is a property of technical importance, since most of liquids or solutions are measured and handled on the basis of volume . Density data are usually used to estimate the required weight of solutions.

The effect of temperature on the densities of Oppanol B, 150, 200 and 250 in reformate and CMC in water are shown in figures (4.11) through (4.14) respectively. The figures indicate, as it is expected for most liquids, that the polymeric solutions become less dense as the temperature rises. A linear decrease of density with temperature increase was noticed for all considered solutions, it was also noticed, that the temperature dependence of density for CMC in water is less than in the case of Oppanol polymers in reformate solvent.

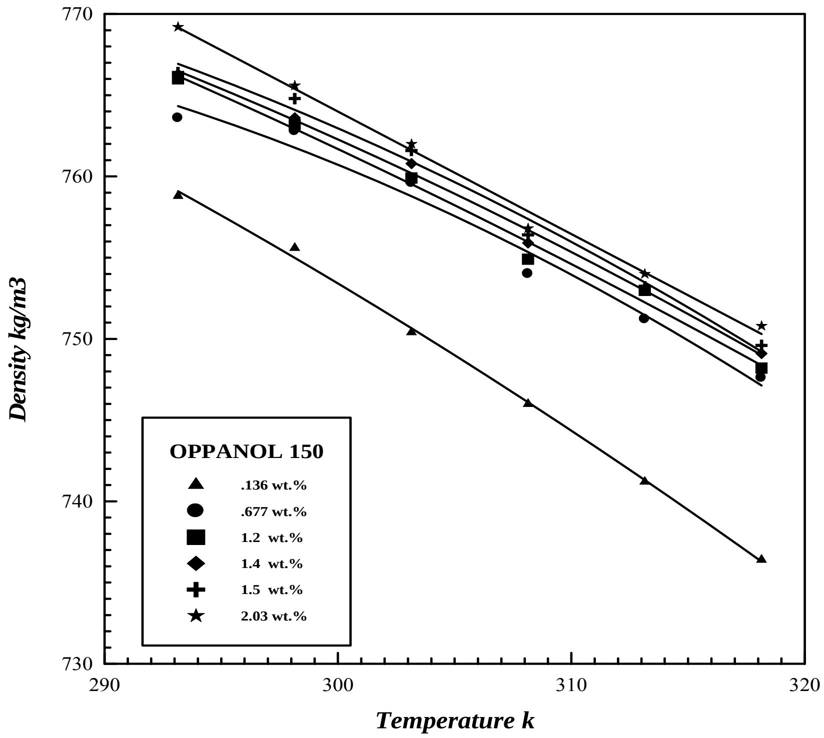


Fig. (4.11) Temp. versus density for Oppanol 150 solutions

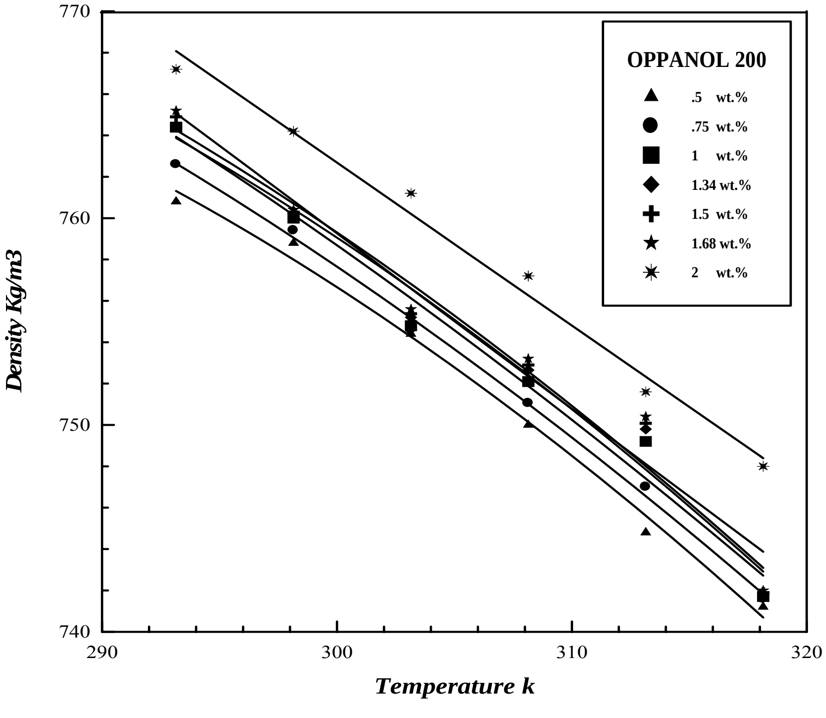


Fig. (4.12) Temp. versus density for Oppanol 200 solutions

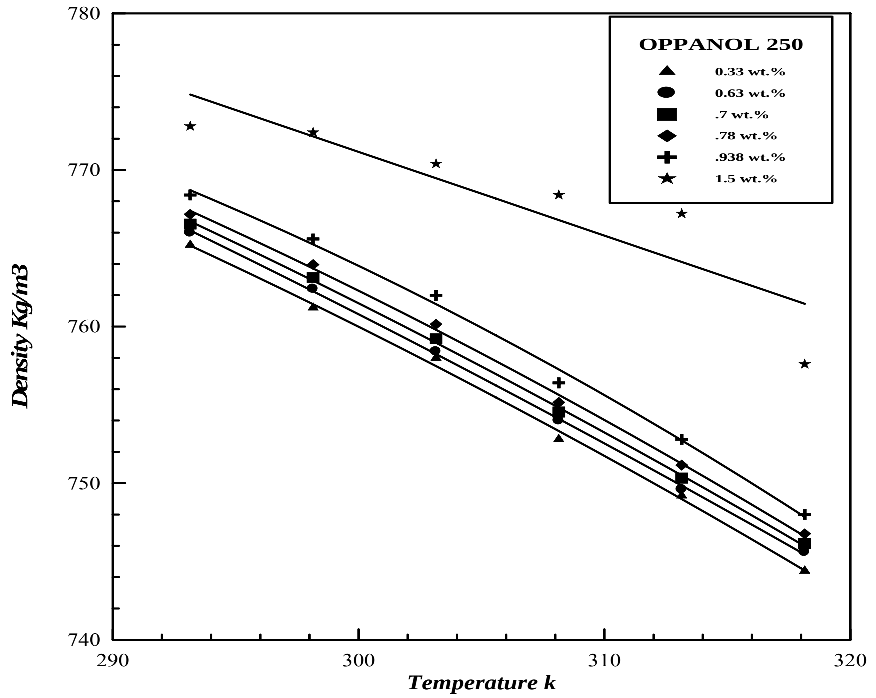


Fig. (4.13) Temp. versus density for Oppanol 250 solutions

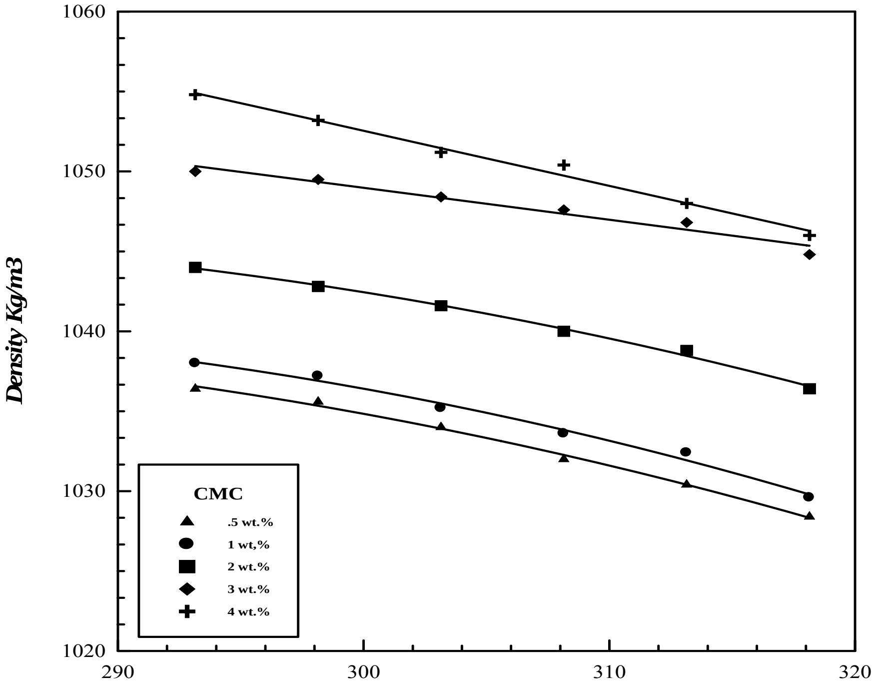


Fig. (4.14) Temp. versus density for CMC solutions

The effect of temperature on density can be also demonstrated for the volume thermal expansion of polymeric solutions. The volume thermal expansion coefficient α (K^{-1}) is defined by equation:

$$\alpha = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P \qquad \text{... (4.1)}$$

Where ρ is the density, T is the temperature, $\left(\frac{\partial \rho}{\partial T}\right)_P$ indicates derivatives at constant pressure, V is the volume (Eric Weisstenin 2006). From the above equation we can draw between thermal expansion coefficient α and temperature for the four types of the polymer solutions used in this study as illustrated in figures (4.15) to (4.18). The figures show a linear increase in thermal expansion coefficient with temperature increase, which is an inverse relationship as in the case of temperature dependence of density.

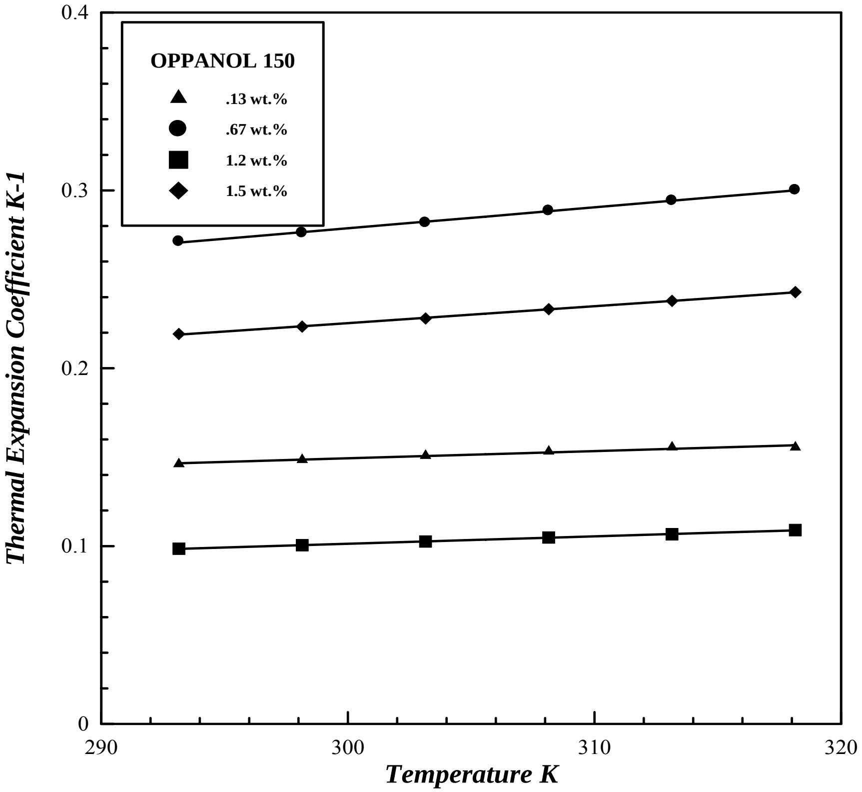


Fig. (4.15) Temp. versus thermal expansion coefficient for Oppanol 150 solutions

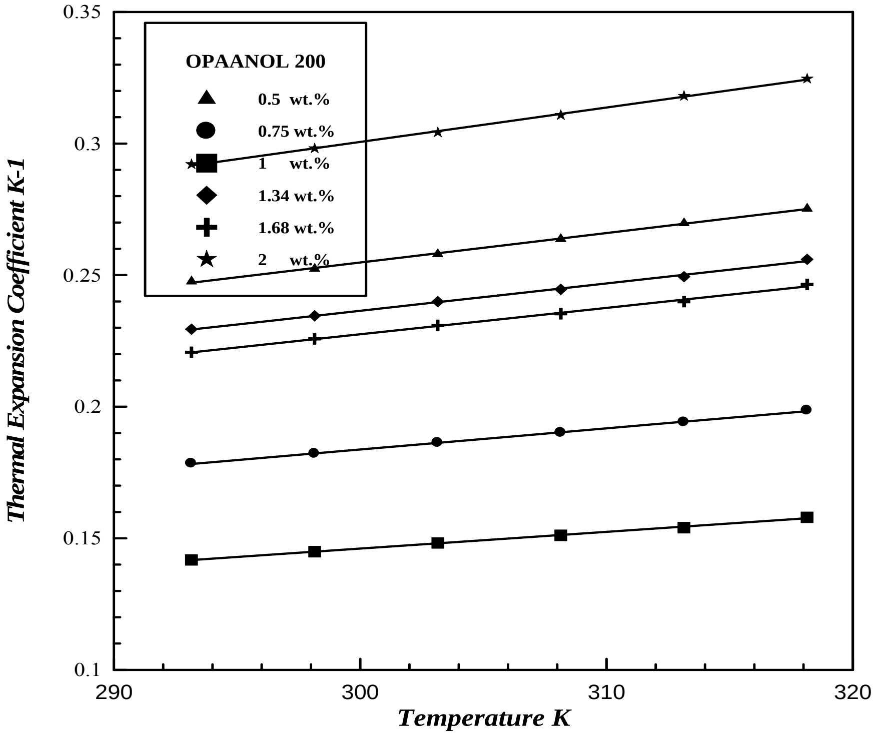


Fig. (4.16) Temp. versus thermal expansion coefficient for Oppanol 200 solutions

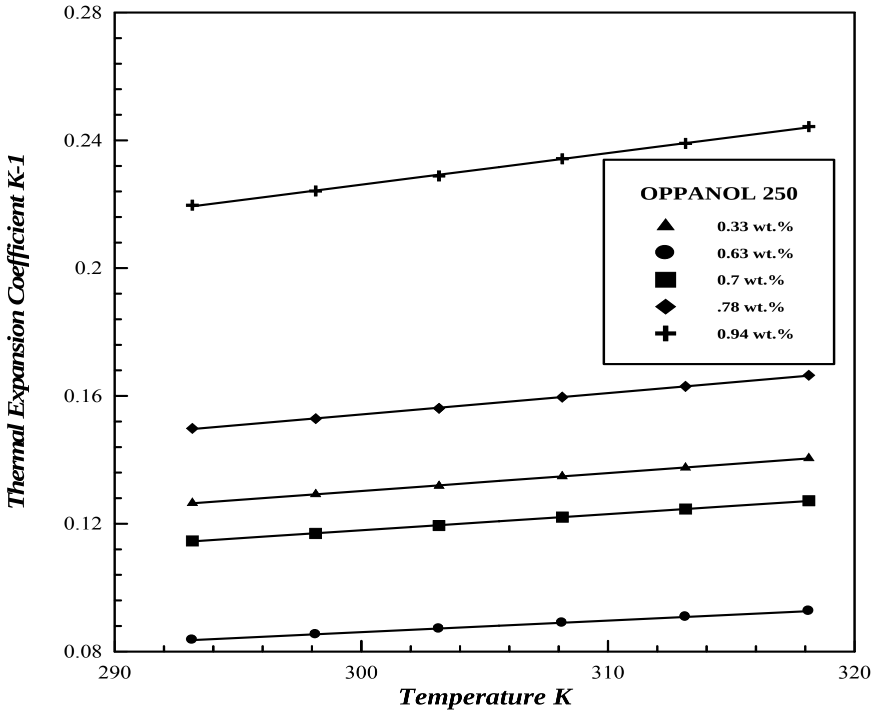


Fig. (4.17) Temp. versus thermal expansion coefficient for Oppanol 250 solutions

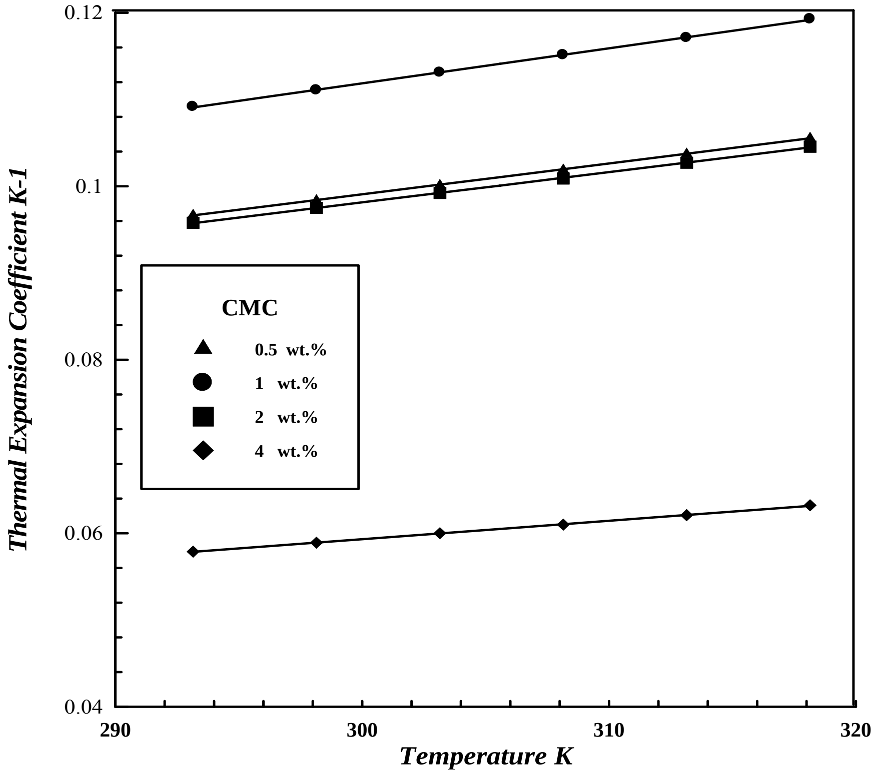


Fig. (4.18) Temp. versus thermal expansion coefficient for CMC solutions

4.4 Testing of Oppanol Polymers as Drag Reducers

4.4.1 Introduction

The aim of the laboratory experiments was to evaluate the drag- reducing effectiveness of various polymers. Oppanol B types, 150, 200 and 250 of different molecular weight were tested in gas oil flow loop at concentrations that might have been economically feasible for commercial applications (Shaker 1987). A 0.03175 m nominal diameter test loop was used to perform the laboratory screening of the drag effectiveness. It was designed to provide turbulent flow, which is required for such investigations. The testing section was (2 m) long and it was away from the entrance length to restrict the pressure drop measurements in the fully developed region. The minimum entrance length, Le was about (1.6 m) and was calculated by the relationship suggested by Desissler (Desissler 1950), as follows

$$Le = 50 \times D \qquad \ldots(3.3)$$

Calibration of the laboratory test loop was performed with untreated gas oil prior to testing and drag –reduction additives. Figure (4.19) shows the calibration pressure drop data for the pipe used at laboratory temperature.

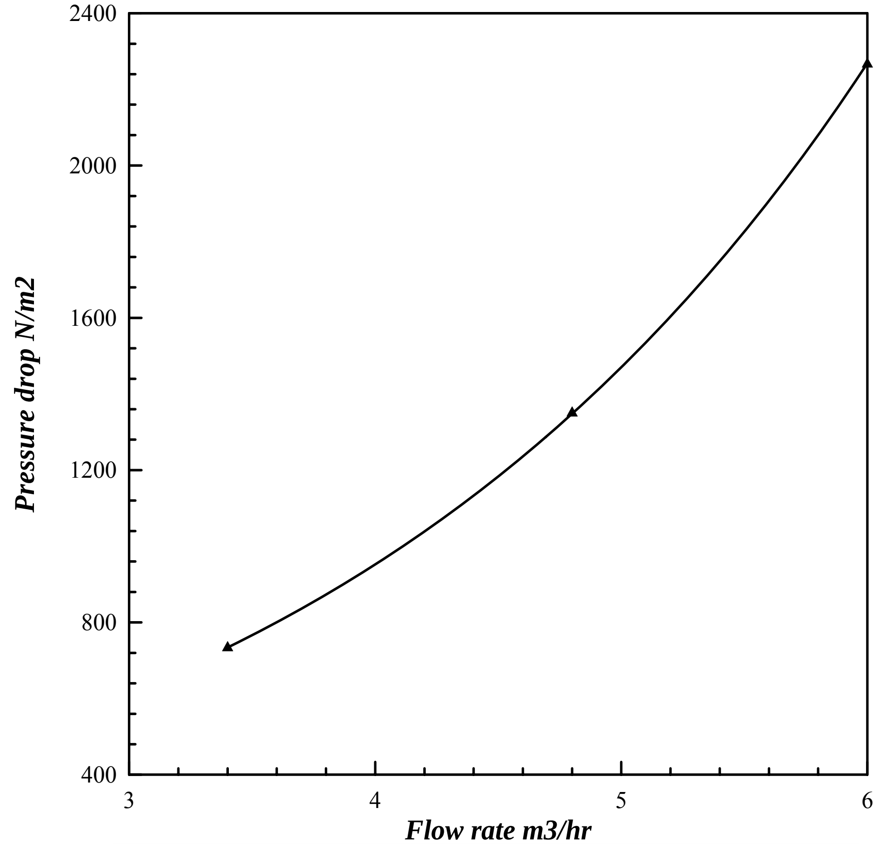


Fig. (4.19) Laboratory test loop calibration data for gas oil

The effectiveness of polymers as drag-reducing additives was examined by measuring the pressure drop-flow rate relationship.

Percentage drag-reduction, % DR is calculated by using equation (2.1)

$$\%DR. = \frac{\Delta P_{untreated} - \Delta P_{treated}}{\Delta P_{untreated}} * 100 \qquad \text{… (2.1)}$$

The drag- reduction data obtained in present investigation has been used to estimate the throughput percent increase, % TI which is calculated by equation (4.3) (GTA-BASF 1985)

$$\%TI = \left(\frac{1}{(1 - \frac{\%Dr}{100})^{0.55}} - 1 \right) * 100 \qquad \text{…. (4.2)}$$

Furthermore, it was worthy to demonstrate the obtained pressure drop data in the form of fanning friction factor, using the following equation (4.3) (Thiel 1989)

$$f = \frac{\Delta P . D / 4L}{\rho . U^2 / 2} \qquad \text{… (4.3)}$$

Where ΔP represents the drop between the upstream and downstream points in the test section and, ρ is gas oil density.

4.4.2 Effect of Concentration

Figures (4.20), (4.21) and (4.22) show the percentage drag reduction as a function of concentration for the three types of Oppanol B additives, namely, 150, 200, and 250 respectively using three flow rates of gas oil. The results showed, that within the range of additives concentrations, (15-50) ppm, a gradual increase of percentage drag reduction was observed by increasing the concentration within certain Reynolds number and that means increasing the turbulence spectrum that is under the drag reducer effect. Furthermore, figures (4.20-4.21) indicate that the percentage drag reduction was noticeably affected by molecular weight.

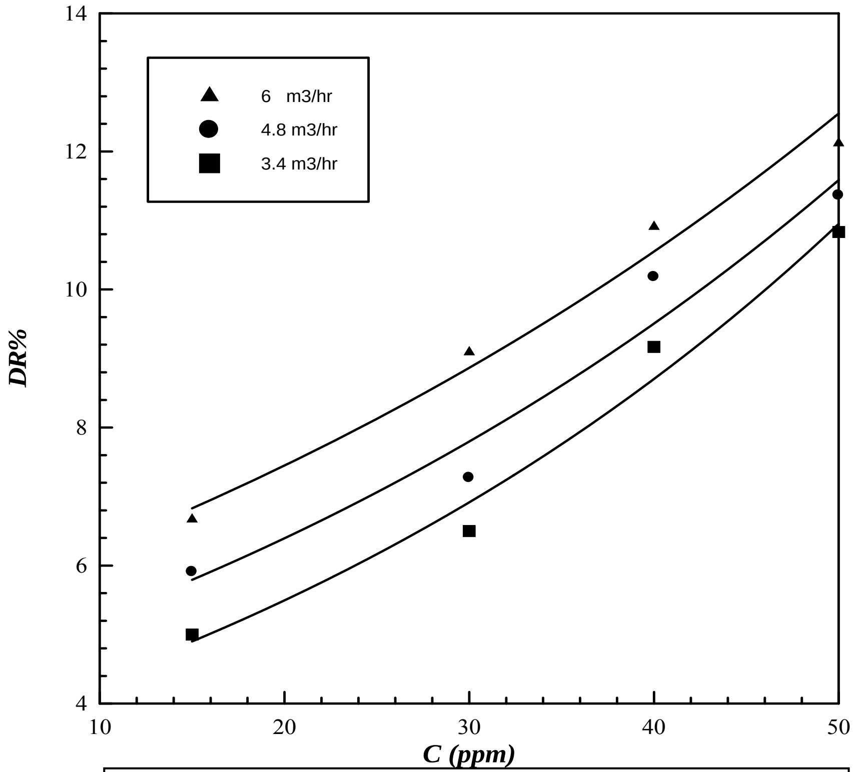


Fig. (4.20) Effect of concentration on percent drag reduction for Oppanol 150

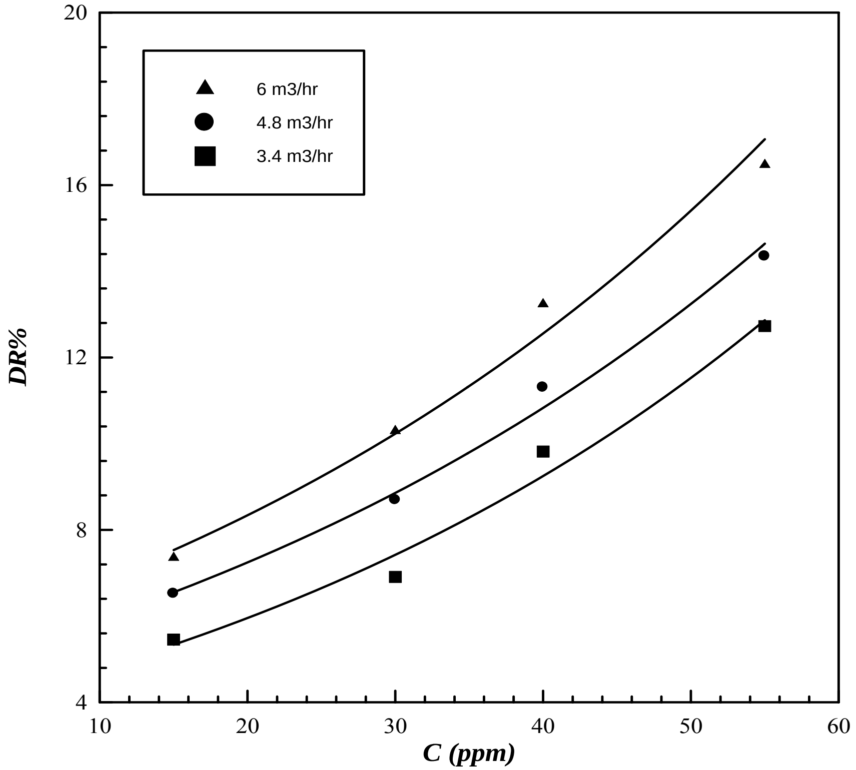


Fig. (4.21) Effect of concentration on percent drag reduction for Oppanol 200

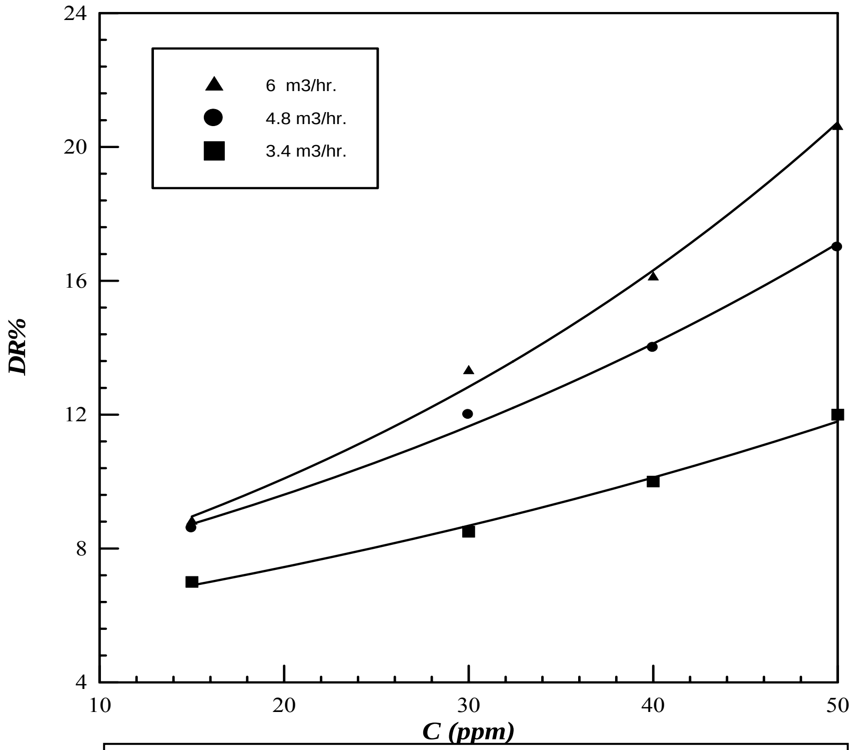


Fig. (4.22) Effect of concentration on percent drag reduction for Oppanol 250

Table (4.2) summarized the results of the effect of both molecular weight and concentration upon drag reduction effectiveness, by choosing the minimum and maximum value of considered concentrations for the comparison. Thus, about 21% drag reduction was achieved by using 50 ppm Oppanol B 250, while the values for lower molecular weight polymers, 200 and 150 were about 16.5% and 12% respectively at the same operating conditions. It can be concluded, that Oppanol B 250 of $5.9*10^6$ g/mole molecular weight is the most efficient drag reducing additive for gas oil flow under turbulent condition.

Throughput increase is a more practical term to investigate the effectiveness of Oppanol polymers on pipelining of gas oil. Figures (4.23), (4.24) and (4.25) show the effect of polymeric concentration on percentage throughput increase for the three Oppanol polymers types 150, 200 and 250 respectively. These figures indicate that throughput increase is a function of both concentration and molecular weight of the additive. The trend of these effects on % TI is approximately similar to their effect on percentage drag reduction.

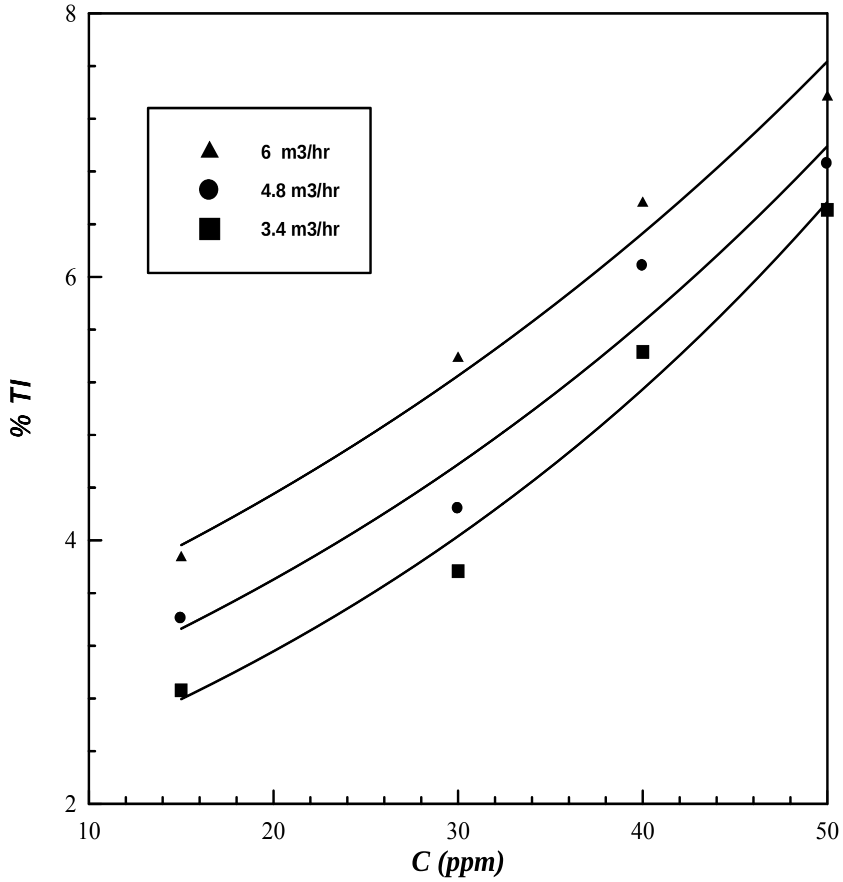


Fig. (4.23) Effect of concentration on percent throughput increase for Oppanol 150

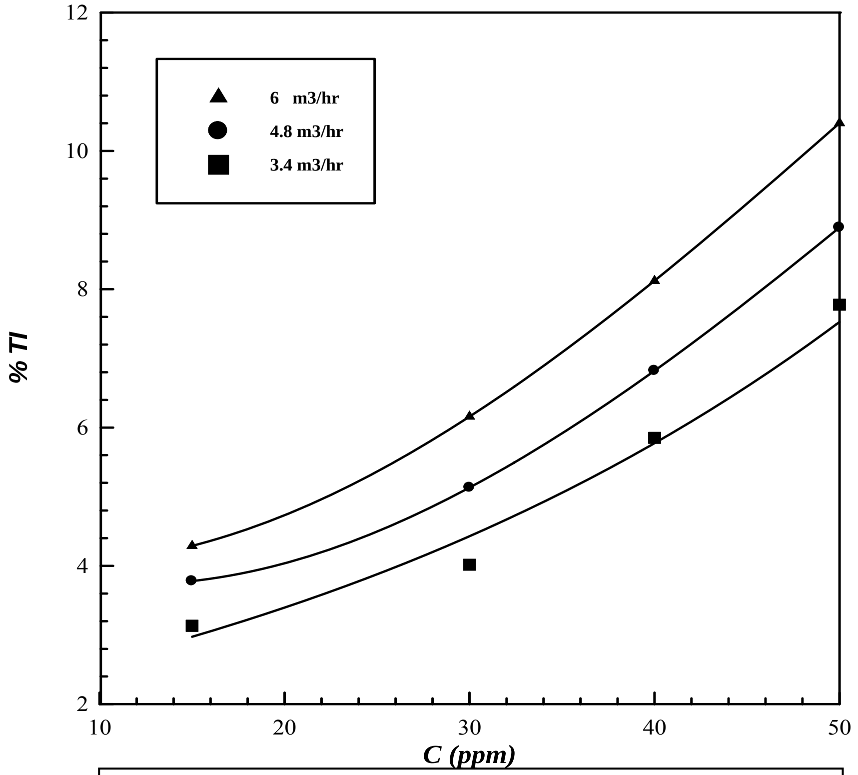


Fig. (4.24) Effect of concentration on percent throughput increase for Oppanol 200

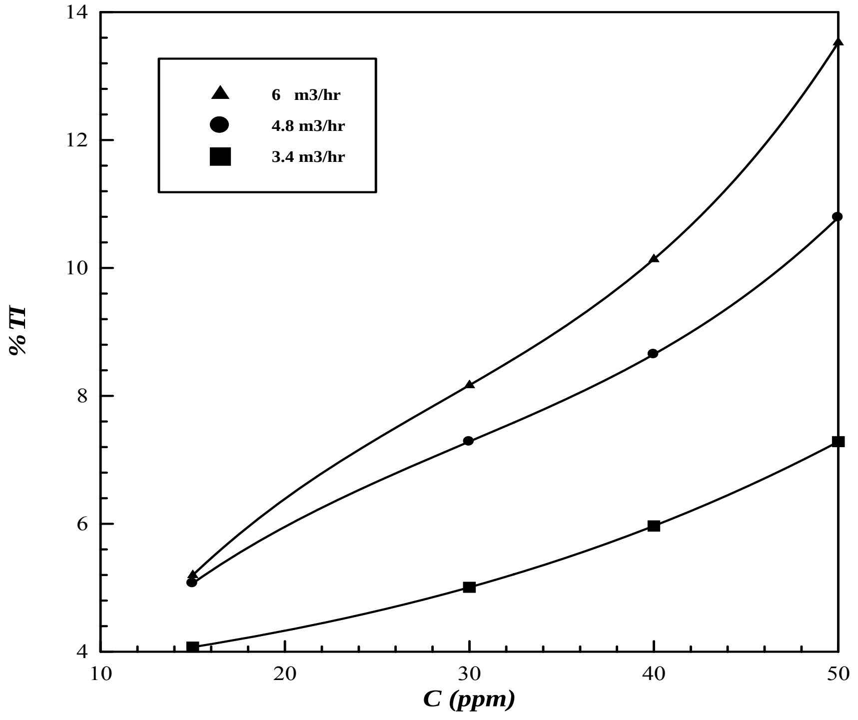


Fig. (4.25) Effect of concentration on percent throughput increase for Oppanol 250

Table (4.2) illustrates some results of percentage throughput increase at two selected concentrations for all Oppanol B types. Oppanol B 250 of molecular weight $5.9*10^6$ g/mole consider to be the more effective additives, reaching about 13.5 % throughput increase at 50 ppm concentration and 6 m^3/hr flow rate of gas oil as listed into appendices.

Table (4.2) Effect of Concentration of Oppanol B Types on %DR and %TI at 6 m^3/hr Flow rate

Polymer Conc.(ppm)	Oppanol B 150		Oppanol B 200		Oppanol B 250	
	%DR	%TI	%DR	%TI	%DR	%TI
15	6.66	3.86	7.35	4.28	8.8	5.19
50	12.12	7.36	16.47	10.4	20.6	13.5

4.4.3 Effect of Flow rate

One of the interesting factors in the study of drag reduction is the effect of flow rate on percent drag reduction and its relation to the turbulence and the effectiveness of the drag reducer additives. Three different flow rates of 3.4, 4.8, and 6 m^3/hr were chosen to study this effect for the Oppanol additives at different concentrations. The results are represented in figures (4.26), (4.27) and (4.28) for Oppanol B 150, 200 and 250 respectively.

Figures (4.26 to 4.28) show that the percent drag reduction is increased as flow rates increase. Increasing the flow rate means increasing the velocity which was represented by the dimensionless form of Reynolds number (Re) that means increasing the degree of turbulence inside the pipe; this will provide a better media to the drag reducer (polymer) to be more effective.

However, it is well known that the dependence of drag- reduction efficiency to be a function of the degree of turbulence (Kulicke and Kotter 1989).

Furthermore, analyzing the results in figures (4.26) through (4.28) show clearly the fact that the dependence of drag- reducing efficiency is a function of polymer molecular weight, polymer concentration and the degree of turbulence. Therefore the highest percentage drag reduction of about 21% was achieved by using Oppanol B 250 ($Mw=5.9*10^6$ g/mole) at 50 ppm concentration and 6 m^3/hr flow rate, which are the extreme conditions within the considered range, as shown in table (4.2).

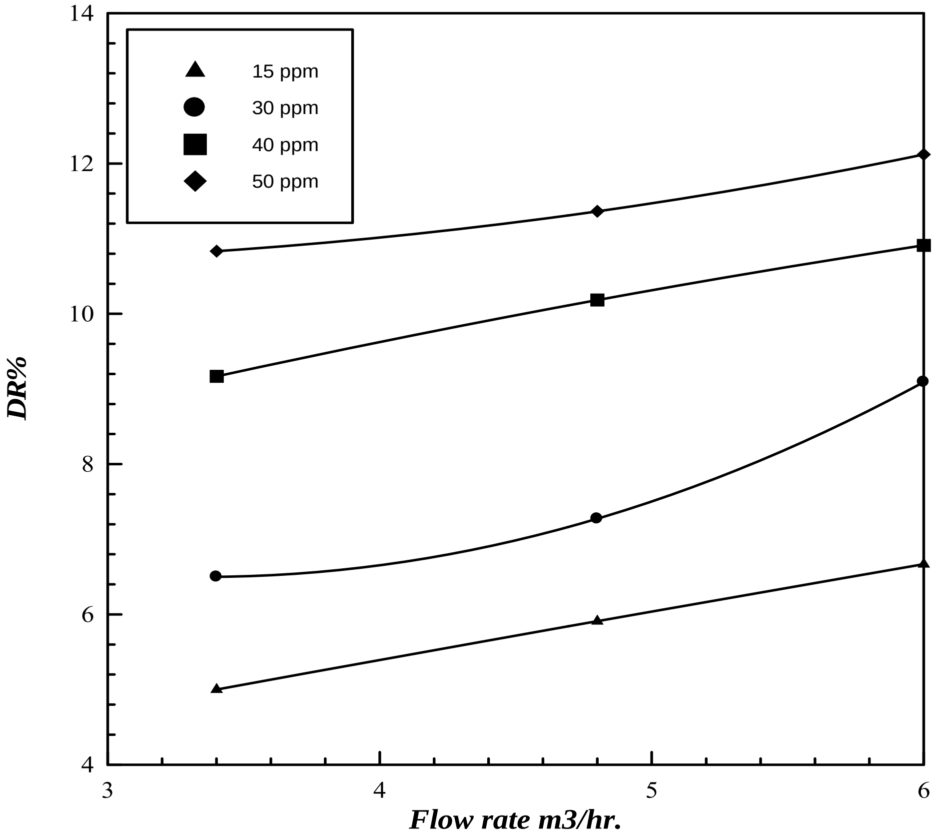


Fig. (4.26) Effect of flow rate on percent drag reduction for Oppanol 150

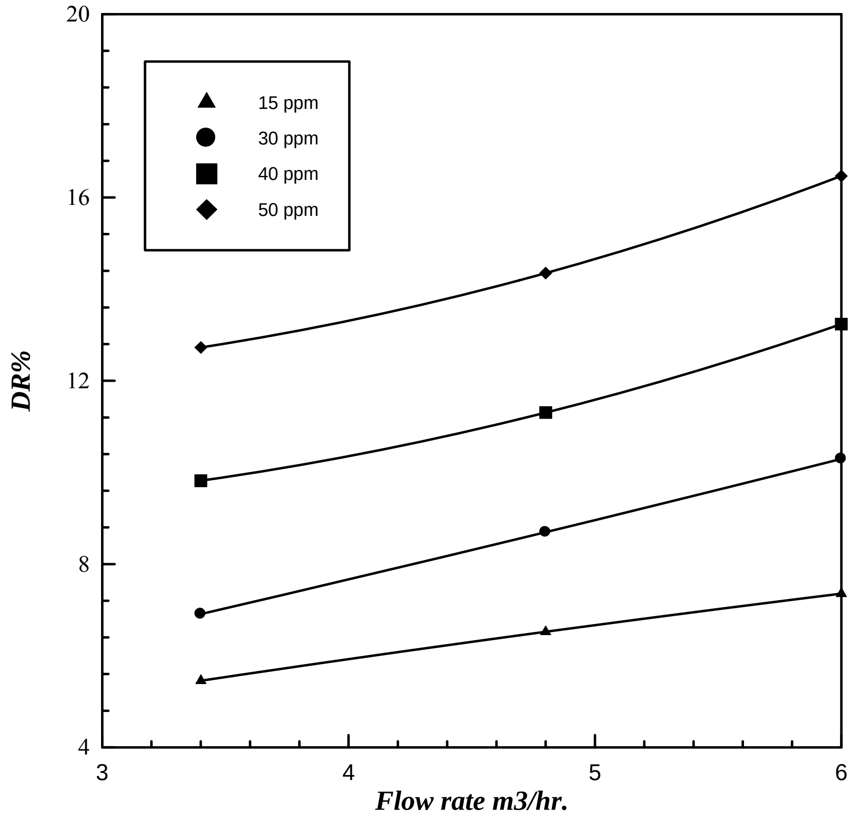


Fig. (4.27) Effect of flow rate on percent drag reduction for Oppanol 200

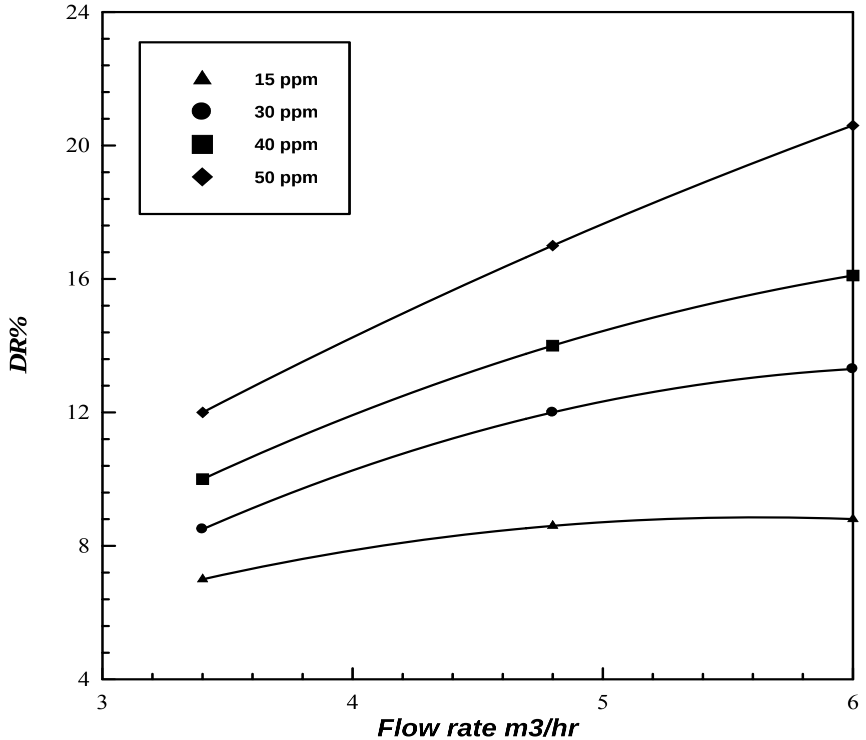


Fig. (4.28) Effect of flow rate on percent drag reduction for Oppanol 250

4.4.4 Friction Factor

Another representation to the effect of all variable used in this investigation can be seen using friction factor which was calculated from equation (3.4).

The effect of polymer additives does not appear in the laminar and transitional regions but in the turbulent region.

Laminar flow region (Re < 2300), where the friction factor follows Poisuelle's law as follows (Virk 1975):

$$f = \frac{16}{\mathrm{Re}} \qquad \dots (4.4)$$

Transition region (Re=2300-3000), where the flow change from laminar to turbulent flow, in which friction coefficient rises rapidly.

Turbulent region (Re > 3000), where the friction factor follows Blasius law:

$$f = 0.0791\ Re^{-0.25} \qquad \dots (4.5)$$

Virk asymptote region, which is suggested by Virk to represent the greatest possible fall in resistance in which the relation between friction factor (*f*) and Reynolds number (Re). The formula for Virk is:

$$f = 0.59\ Re^{-0.58} \qquad \dots (4.6)$$

Selected samples of the experimental results for friction factor are shown in figures (4.29) to (4.31). These figures show the friction factor versus Reynolds number for 0.03175 m pipe diameter, various polymer types and polymer concentrations.

These figures summarize all the effect of the variables used in the present investigation. It shows that the friction factor decreases by increasing the additive concentration, molecular weight of polymer and Reynolds number as listed into appendices. It is clear that increasing the concentration of polymer solution causes decreasing of friction factor up to the Virk asymptote line (Spalding 1967).

It can be noticed that, when the polymer concentration is zero (pure solvent), most of the experimental data points are located close to Blasuis asymptote. When the polymer is presented in the flow, the experimental data points are positioned in the direction of lowering friction towards Virk asymptote that represents the maximum limits of drag reduction, which will give the idea that, to reach such asymptote, higher additive concentration and Reynolds number are needed. But, it must be considered that higher concentrations should not affect solvent properties, also by considering the economical costs of the raw materials of drag reducing agents, therefore it was difficult to reach Virk asymptote without affecting the investigated solvent properties.

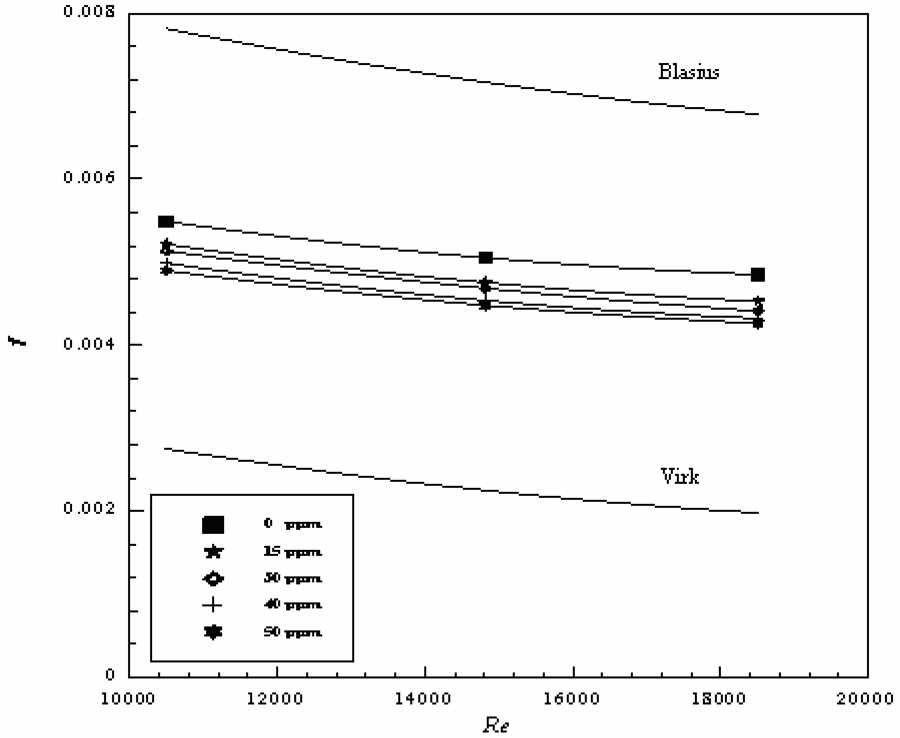


Fig. (4.29) The friction factor as a function of Reynolds number for Oppanol 150

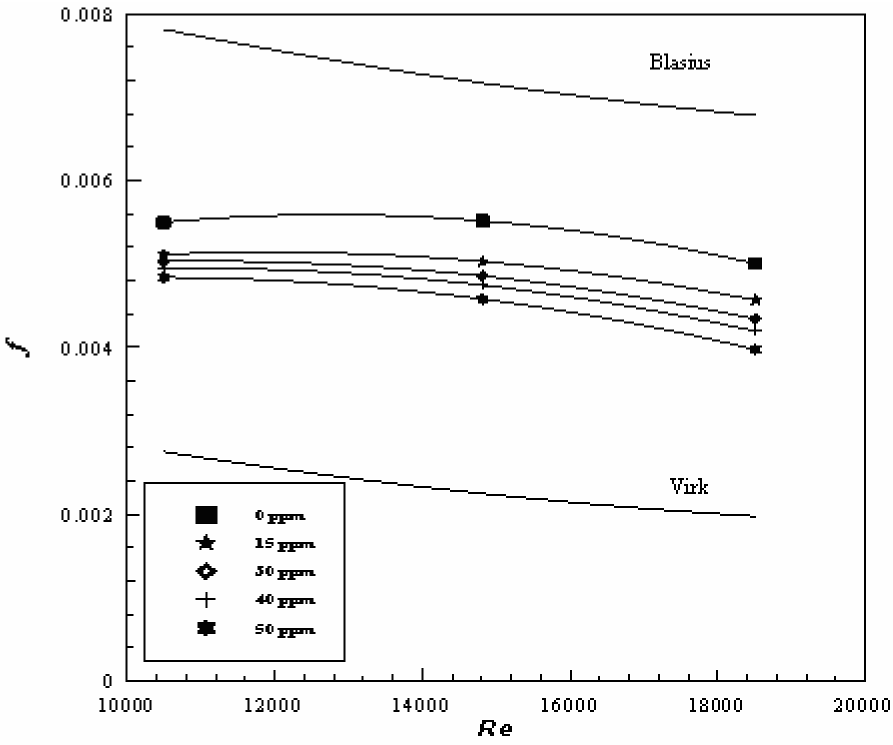


Fig. (4.30) The friction factor as a function of Reynolds number for Oppanol 200

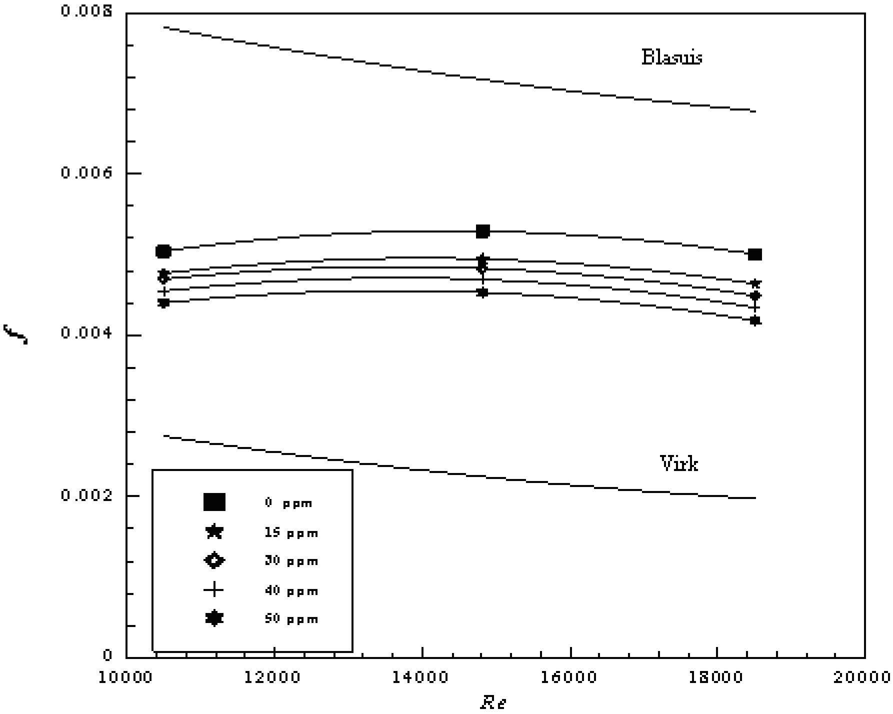


Fig. (4.31) The friction factor as a function of Reynolds number for Oppanol 250

4.5 Testing of CMC as Drag-Reducer

Carboxymethylcellulose, CMC of a molecular weight, $0.4*10^6$ g/mole, was tested in a water flow loop at different concentrations and liquid flow rates (Deshmukh 1990).Calibration of flowing system was done with untreated tap-water prior to testing experiments. Figure (4.32) shows the pressure drop data for the 1.25 inch (0.03175 m) pipe diameter used at laboratory temperature.

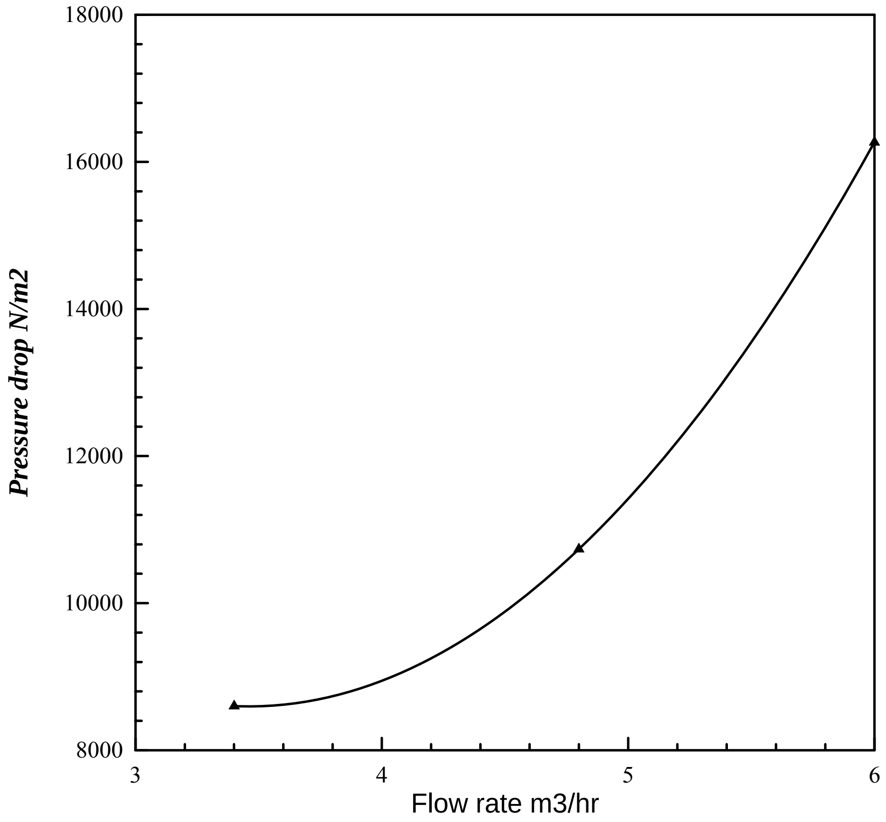


Fig. (4.32) Laboratory test loop calibration data for water

Figure (4.33) illustrate the effect of CMC concentration of 70 ppm on the percentage increase in drag reduction, while figure (4.34) show the resulted throughput increase. It can be observed that the CMC concentration enhances both the percentage drag reduction and throughput increase. Higher concentrations in the range of (50-70) ppm are more efficient.

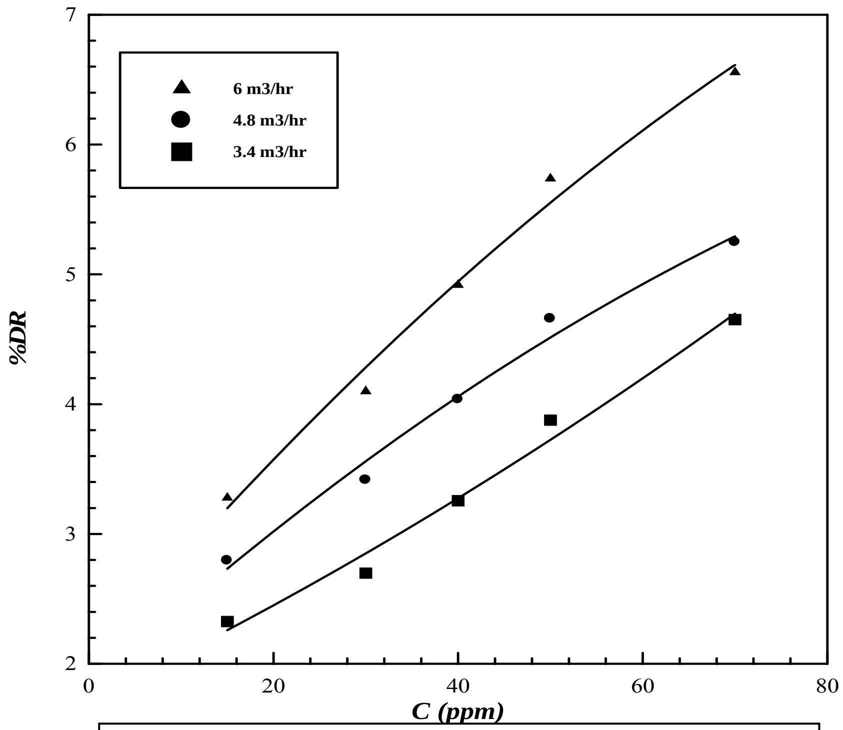


Fig. (4.33) Effect of concentration on percent drag reduction for CMC

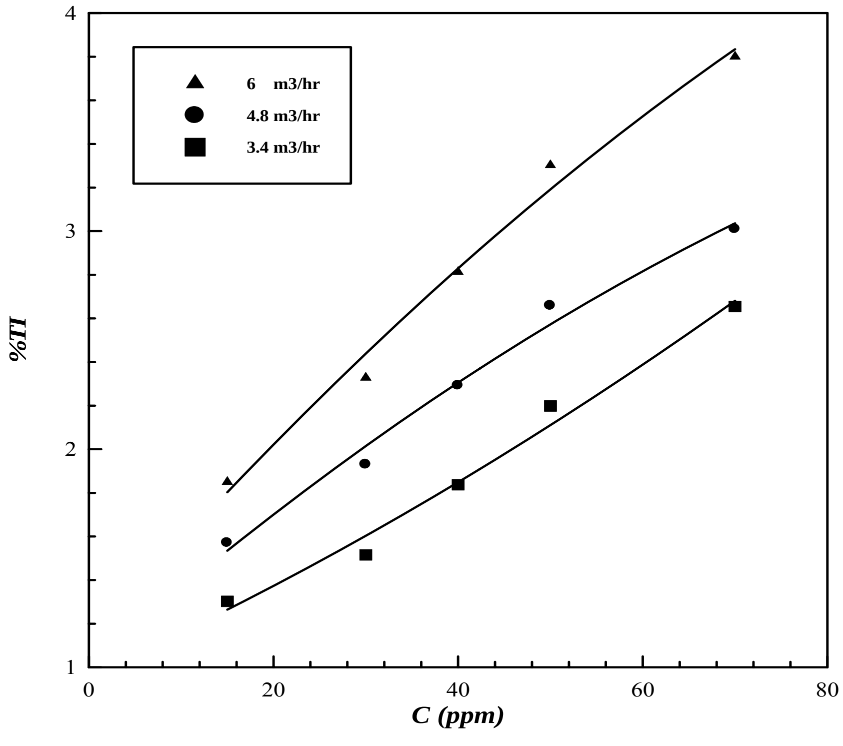


Fig. (4.34) Effect of concentration on percent throughput increase for CMC

The effect of flow rate on the performance of CMC as a drag reducer was conducted for three different flow rates, 3.4, 4.8 and 6 m^3/hr as illustrated in figures (4.35) and (4.36) for percentage drag reduction and throughput increase respectively. The results indicate that an increase in flow rate (increase of turbulence) improves the effectiveness of CMC noticeable.

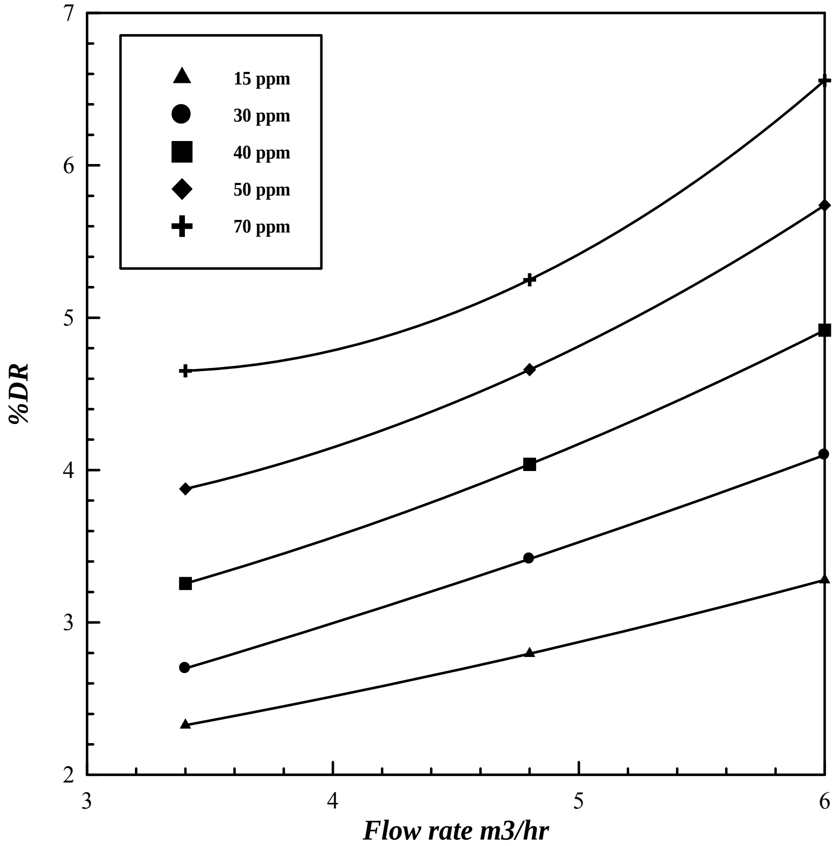


Fig. (4.35) Effect of flow rate on percent drag reduction for CMC

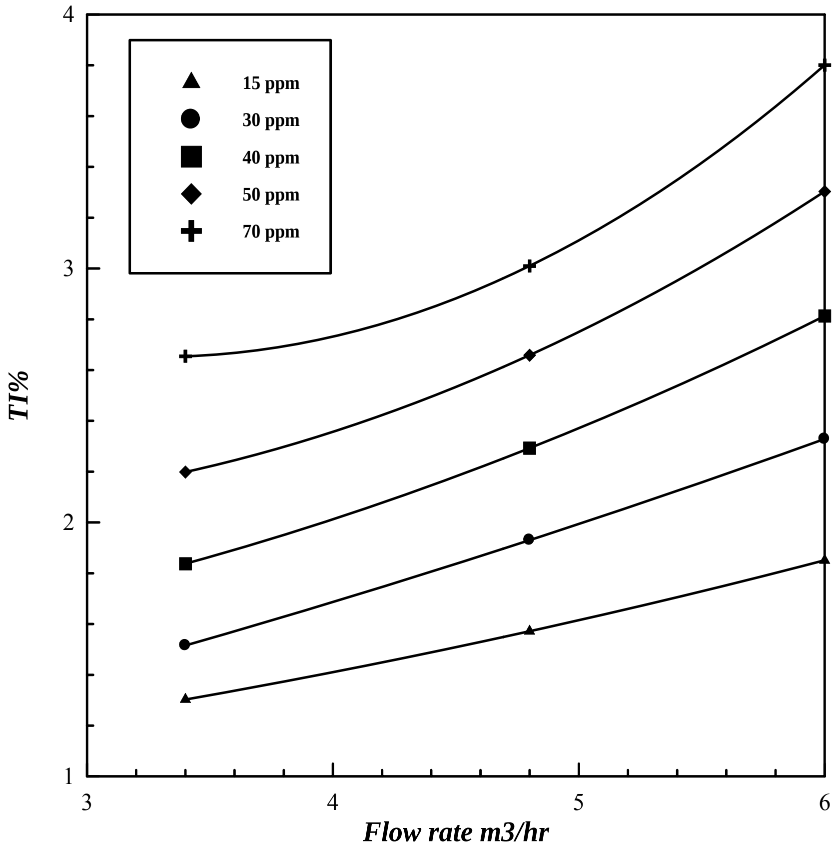


Fig. (4.36) Effect of flow rate on percent throughput increase for CMC

The results illustrated in figures (4.32) through (4.36) are in good agreement with the results obtained by other researchers by using CMC drag reducer (Gadda 1985) (Ali 1996) (Deshmukh 1990).

Chapter Five

Conclusions and Recommendations

5.1 Conclusions

1. Reformate of (80-200) ºC boiling range and about 50% aromatic content is considered to be a suitable solvent for the high molecular weight polyisobutylenes of Oppanol B type. The dependence of dissolving is a function of their molecular weight.
2. Maximum 2 wt. % concentration of homogenous and stable solutions were obtained at two, three and five days for Oppanol B 150 < ($Mw=2.6*10^6$ g/mol), 200 ($Mw=4.1*10^6$ g/mol) and Oppanol 250 ($Mw=5.9*10^6$ g/mol) respectively in a shaker at room temperature. 4 wt. % homogenous at and stable CMC solutions were produced at 24 hr shaking time.
3. The drag-reduction efficiency of various reformate solutions of Oppanol polymers was examined in gas oil flow loop. The results show that the considered polymeric solutions are effective in turbulent drag reduction. The efficiency is affected by polymer concentration and molecular weight and higher level of turbulence.
4. The prepared Oppanol B 250 solutions can be considered as an efficient drag- reducer at concentrations up to 50 ppm in turbulent pipelining of crude oils and fractions.

5.2 Recommendations

1. Further work can be carried out to prepare solutions of other types of drag-reducer, such as polyethyleneoxide and polyacrylamide as water soluble polymer in addition to studying their rheological properties.
2. Studying the effect of temperature up to 70°C and combined type of solvents on the dissolving of drag reducer polymers.
3. An attempt can be made to evaluate the stability of polymeric additive solutions towards their molecular degradation by shear stress, elevated temperature and energetic radiation.
4. Investigating the effect of mechanical stresses and time on the effectiveness of high molecular polymers as drag- reducers under turbulent flow.

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Appendices

Table (A-1) Experimental Results for Oppanol 150 as Drag Reducer in Gas Oil

Flow rate m^3/hr	Conc. ppm	Δp N/m2	% DR	%TI	Friction factor
3.4	0	799.9800	-	-	0.005497
	15	759.9810	5.00000	2.86100	0.005222
	30	747.9813	6.50000	3.76600	0.005139
	40	726.6485	9.166667	5.43000	0.004993
	50	713.3155	10.83333	6.51000	0.004901
4.8	0	1466.60	-	-	0.005056
	15	1380.00	5.909091	3.40700	0.004757
	30	1360.00	7.272727	4.24000	0.004688
	40	1317.30	10.18182	6.08400	0.004541
	50	1300.00	11.36364	6.86000	0.004482
6	0	2199.95	-	-	0.004854
	15	2053.28	6.666667	3.867523	0.00453
	30	1999.95	9.090909	5.381888	0.004413
	40	1959.95	10.90909	6.559368	0.004324
	50	1933.29	12.12121	7.365257	0.004266

Table (A-2) Experimental Results for Oppanol 200 as Drag Reducer in Gas Oil

Flow rate m^3/hr	Conc. ppm	Δp N/m2	% DR	% TI	Friction factor
3.4	0	733.315	-	-	0.005039
	15	693.316	5.455	3.133	0.004764
	30	682.6496	6.909	4.016	0.004691
	40	661.3168	9.818	5.848	0.004544
	50	639.984	12.73	7.775	0.004397
4.8	0	1533.295	-	-	0.005286
	15	1433.298	6.522	3.779	0.004941
	30	1399.965	8.696	5.131	0.004826
	40	1359.966	11.3	6.820	0.004688
	50	1313.301	14.35	8.891	0.004528
6	0	2266.610	-	-	0.005001
	15	2099.948	7.353	4.290	0.004633
	30	2033.283	10.29	6.157	0.004486
	40	1966.618	13.24	8.121	0.004339
	50	1893.286	16.47	10.40	0.004177

Table (A-3) Experimental Results for Oppanol 250 as Drag Reducer in Gas Oil

Flow rate m^3/hr	Conc. ppm	Δp N/m2	% DR	%TI	Friction factor
3.4	0	800	-	-	0.005497
	15	744	7	4.072	0.005112
	30	732	8.5	5.007	0.005029
	40	720	10	5.966	0.004947
	50	704	12	7.284	0.004837
4.8	0	1600	-	-	0.005516
	15	1459	8.6	5.070	0.005029
	30	1408	12	7.284	0.004854
	40	1376	14	8.649	0.004744
	50	1328	17	10.79	0.004578
6	0	2267	-	-	0.005001
	15	2067	8.8	5.197	0.00456
	30	1967	13.3	8.166	0.004339
	40	1900	16.1	10.14	0.004192
	50	1800	20.6	13.53	0.003971

Table (A-4) Results of Friction Factor for Blasuis and Virk Asymptotes

Re	$f_{Blasuis}$	f_{Virk}
18509.24	0.006782	0.001976
14807.39	0.007171	0.002249
10488.57	0.007816	0.002747

Table (A-5) Experimental Results for CMC as Drag Reducer in Water

Flow rate m^3/hr	Conc. ppm	Δp N/m2	% DR	%TI
3.4	0	8599.785	2.325581	-
	15	8399.79	2.697674	1.302588
	30	8367.791	3.255814	1.51547
	40	8319.792	3.875969	1.837169
	50	8266.46	4.651163	2.198004
	70	8199.795	2.325581	2.654154
4.8	0	10733.07	-	-
	15	10433.07	2.795031	1.571378
	30	10366.41	3.416149	1.930115
	40	10299.74	4.037267	2.292447
	50	10233.08	4.658385	2.658431
	70	10169.75	5.248447	3.009556

Table (A-5) Continue

Flow rate m^3/hr	**Conc. ppm**	**Δp N/m2**	**% DR**	**%TI**
6	**0**	**16266.26**	**-**	**-**
	15	**15732.94**	**3.278689**	**1.850415**
	30	**15599.61**	**4.098361**	**2.328282**
	40	**15466.28**	**4.918033**	**2.812522**
	50	**15332.95**	**5.737705**	**3.303276**
	70	**15199.62**	**6.557377**	**3.80069**

الخلاصة

يعتبر توفر محاليل البوليمرات المقللة للإعاقة حلاً مرناً لزيادة الضخ في الأنابيب الناقلة للنفط الخام و مشتقاته والمياه. إن ذلك يعطي أهمية خاصة لتحضير هذه المحاليل موضوعياً بالإعتماد على مذيبات محلية. تم إختيار ثلاث أنواع من بوليمرات البولي آيزوبيوتيلين (نوع الأوبانول) المجهزة تجارياً، و بأوزان جزيئية مختلفة، علاوة على الكاربوكسي مثيل سيليلوز القابل للإذابة في الماء في هذاالبحث. كما تم إختبار خمسة مذيبات من منتجات نفطية محلية مختلفة وهي النفثا الخفيفة، النفثا الثقيلة، الريفورميت، الصفوة الخاصة و خليط من الزايلينات لعملية إذابة بوليمرات الآيزوبيوتيلين .

من خلال التجارب العملية ، يعد الريفورميت أفضل المذيبات لبوليمرات الأوبانول. تم الحصول على محاليل متجانسة و ثابتة بتركيز ٢% وزناً للبوليمرات خلال يوم الى ثلاثة أيام حسب الوزن الجزيئي بأستخدام الهزاز للرج عند درجة حرارة الغرفة. كما تم الحصول على ٤ % وزناً من مادة كاربوكسي-مثيل سيلليلوز في الماء خلال ٢٤ ساعة رج بالهزاز.

تم إختبار فاعلية تقليل الإعاقة لبوليمرات الآيزوبيوتيلين ذات الأوزان الجزيئية المختلفة (٢,٦ * ١٠^{٦} غرام/مول ، ٤,١*١٠^{٦} غرام/مول ، ٥,٩ * ١٠^{٦} غرام/مول)عند تراكيز و سرع جريان مختلفة في جريان زيت الغاز المضطرب بواسطة مضخة التروس.لقد لوحظ أن كفاءة المضافات تعتمد على التركيز، عدد رينولدز (الأضطراب) و الوزن الجزيئي للبوليمر. لذلك يعد الأوبانول ب ٢٥٠ ذي الوزن الجزيئي ٥,٩ * ١٠^{٦}غرام/مول الأكثر فعالية ضمن البوليمرات قيد الأختبار.

تم حساب معامل الأحتكاك بالأعتماد على النتائج العملية. تقع قيم معامل الأحتكاك لجريان زيت الغاز الغير معامل بإتجاه محاذي بلاسيوس، بينما تتجه نحو محاذي فيرك عند أضافة البوليمرات الى الجريان.

تتمتع أضافة الكاربوكسي مثيل سيلليلوز بفعالية واطئة في تقليل الإعاقة لأنابيب جريان الماء. و بالأمكان إعزاء ذلك الى إنخفاض الوزن الجزيئي و الى طبيعة التركيب الجزيئي للكاربوكسي مثيل سيلليلوز مقارنة ببوليمرات الأوبانول ذات الأوزان الجزيئية العالية جداً و تركيبها الخطي المرن.

شكر و تقدير

أتقدم بجزيل الشكر و الأمتنان و التقدير الى الدكتور الفاضل *جابر شنشول جمالي* لتفضله بالأشراف على هذا العمل لما قدمه لي من أهتمام كبير و توجيهات قيمة.

الشكر الجزيل الى عميد كلية الهندسة والى أساتذتنا الأعزاء في قسم الهندسة الكيمياوية الذين كانوا شمعة أضاءت لنا دروب العلم.

و الشكر الخاص الى عائلتي الكريمة و خاصة الى أختي *الغالية إيناس* (رحمها الله و أسكنها فسيح جناته) لما قدموه لي من تشجيع و دعم كبيرين.

و أخيراً أود أن أقدم تقديري الى أصدقائي و الى جميع من ساعدني عملياً و معنوياً لأتمام هذا العمل، أسأل الله تعالى أن يوفق الجميع لخدمة الوطن و الأنسانية أنه سميع مجيب.

إذابة و إختبار البوليمرات المقللة للإعاقة ذات الوزن الجزيئي العالي

رسالة
مقدمة إلى كلية الهندسة في جامعة النهرين
و هي جزء من متطلبات نيل درجة ماجستير علوم
في الهندسة الكيمياوية

من قبل
حلا صلاح الدين مهدي الشفي
بكالوريوس في الهندسة الكيمياوية

جمادى الأخرة ١٤٢٧

حزيران ٢٠٠٦