

1. Introduction:

1.1 Plant gum:

Gum arabic, also known as **acacia gum**, is a natural gum made of the hardened sap of various species of the acacia tree. Originally, gum arabic was collected from *Acacia nilotica* which was called the "Gum arabic tree"; in the present day, gum arabic is predominantly collected from two related species, namely *Acacia senegal*^[2] and *Vachellia (Acacia) seyal*. Producers harvest the gum commercially from wild trees, mostly in Sudan (80%) and throughout the Sahel, from Senegal to Somalia—though it is historically cultivated in Arabia and West Asia.

Gum arabic is a complex mixture of glycoproteins and polysaccharides. It is the original source of the sugars arabinose and ribose, both of which were first discovered and isolated from it, and are named after it.

Gum arabic is used primarily in the food industry as a stabilizer. It is edible and has E number E414. Gum arabic is a key ingredient in traditional lithography and is used in printing, paint production, glue, cosmetics and various industrial applications, including viscosity control in inks and in textile industries, though less expensive materials compete with it for many of these roles.

While gum arabic is now produced throughout the African Sahel, it is still harvested and used in the Middle East. For example, Arab populations use the natural gum to make a chilled, sweetened, and flavored gelato-like dessert.

1.2 Definition:

Gum arabic was defined by the 31st Codex Committee for Food Additives, held at the Hague, Holland, from 19–23 March 1999, as the dried exudate from the trunks

and branches of *Acacia senegal* or *Vachellia (Acacia) seyal* in the family Leguminosae (Fabaceae)”.

1.3 Usage:

Gum arabic's mixture of polysaccharides and glycoproteins gives it the properties of a glue and binder that is edible by humans. Other substances have replaced it where toxicity is not an issue, as the proportions of the various chemicals in gum arabic vary widely and make it unpredictable. Still, it remains an important ingredient in soft drink syrups, "hard" gummy candies such as gumdrops, marshmallows, M&M's chocolate candies—and edible glitter, a popular modern cake-decorating staple. For artists, it is the traditional binder in watercolor paint, in photography for gum printing, and it is used as a binder in pyrotechnic compositions. Pharmaceutical drugs and cosmetics also use the gum as a binder, emulsifying agent, and a suspending or viscosity increasing agent. Wine makers have used gum arabic as a wine fining agent.

It is an important ingredient in shoe polish, and can be used in making homemade incense cones. It is also used as a lickable adhesive, for example on postage stamps, envelopes, and cigarette papers. Lithographic printers employ it to keep the non-image areas of the plate receptive to water. This treatment also helps to stop oxidation of aluminium printing plates in the interval between processing of the plate and its use on a printing press. (<https://en.wikipedia.org/wiki/Gum>)

1.4 Polyacantha tree:

Gum from Acacia Polyacantha tree.

Classification of Acacia Polyacantha, tree.

Family: leguminosae.

Subfamily: Mimosaceae

Genus: Acacia

Species: Polyacantha

English name: Falcon's claw acacia

Arabic name: Kakamut, umsiniena

1.5 General distribution:

Polyacantha are dispersed throughout tropical Africa. In Sudan, there are several regional varieties, which usually occur along rivers and valleys where the water table is fairly high, and the soils are good.

1.5.1 Description:

This tree occasionally reaches 20m in height and trunk can be 70cm in diameter. A knobby bark and paired thorns are its most conspicuous features. The bark is yellowish with born scale and black knots in the place of former leaves and thorns. Thorns occur in pairs and are sharply curved; they are brown with black tips. Leaves may reach 25cm in length, are biparipinnate with 10-40 pairs of pinnae and 35-60 of leaf each. A prominent gland is present at the base of the leaf. Flowers occur in pairs or 3 spicate racemes from the leaf axils and are cream colored and strongly scented. Fruits consist of pods up to 15 cm long, which each contain 5-9 seeds.

1.5.2 Uses:

The woods is used mainly in fuel and charcoal of good quality, fence posts, farm implements, railway; sleeper, beams and rafters. The gum is edible and uses as adhesive in the treatment of textile fibers. The roots is said to act as a general health tonic as and antidote for snake bite, and cure for venereal diseases, preparation from the bark is used for general stomach disorders. (Omer.E.A, 2004)

1.6 Solution Viscosity and Molecular Size:

The usefulness of solution viscosity as a measure of polymer molecular weight has been recognized ever since the early work of Staudinger (1930). Solution viscosity is basically a measure of the size or extension in space of polymer molecules. It is empirically related to molecular weight for linear polymers; the simplicity of the measurement and the usefulness of the viscosity-molecular weight correlation are so great that viscosity measurement constitutes an extremely valuable tool for the molecular characterization of polymers.

1.6.1 Experimental methods:

Measurements of solution viscosity are usually made by comparing the efflux time t required for a specified volume of polymer solution to flow through a capillary tube with the corresponding efflux time t_0 for the solvent. From t, t_0 , and the solute concentration are derived several quantities whose defining equations and names are given in Table 1-1. Two sets of nomenclature are in use for these quantities; one (Cragg 1946) has had long.

Table 1-1 Nomenclature of solution viscosity:

Common Name	Recommended Name	Symbol and Defining Equation
Relative viscosity	Viscosity ratio	$\eta_r = \eta/\eta_o \simeq t/t_o$
Specific viscosity	-	$\eta_{sp} = \eta_r - 1 = (\eta - \eta_o)\eta_o$ $\simeq (t - t_o)/t_o$
Reduced Viscosity	Viscosity number	$\eta_{red} = \eta_{sp}/c$
Inherent viscosity	Logarithmic viscosity number	$\eta_{inh} = (\ln \eta_r)/c$
Intrinsic viscosity	Limiting viscosity number	$[\eta] = \left(\frac{\eta_{sp}}{c}\right)_{c=0} = \left[\frac{\ln \eta_r}{c}\right]_{c=0}$

(text book of polymer science, 1970)

1.7 Viscosity:

The **viscosity** of a fluid is a measure of its resistance to gradual deformation by shear stress or tensile stress. For liquids, it corresponds to the informal concept of "thickness"; for example, honey has a much higher viscosity than water.

Viscosity is a property arising from collisions between neighboring particles in a fluid that are moving at different velocities. When the fluid is forced through a tube, the particles which compose the fluid generally move more quickly near the tube's axis and more slowly near its walls; therefore some stress (such as a pressure difference between the two ends of the tube) is needed to overcome the friction between particle layers to keep the fluid moving. For a given velocity pattern, the stress required is proportional to the fluid's viscosity.

A fluid that has no resistance to shear stress is known as an *ideal* or *inviscid* fluid. Zero viscosity is observed only at very low temperatures in superfluids. Otherwise, all fluids have positive viscosity, and are technically said to be viscous or viscid. In common parlance, however, a liquid is said to be *viscous* if its viscosity is substantially greater than that of water, and may be described as *mobile* if the viscosity is noticeably less than water. A fluid with a relatively high viscosity, such as pitch, may appear to be a solid. (<https://en.wikipedia.org/wiki/Viscosity>)

1.8 Intrinsic viscosity:

Intrinsic viscosity $[\eta]$ is a measure of a solute's contribution to the viscosity η of a solution. It should not be confused with **inherent viscosity**, which is the ratio of the natural logarithm of the relative viscosity to the mass concentration of the polymer.

Intrinsic viscosity is defined as

$$[\eta] = \lim_{\phi \rightarrow 0} \frac{\eta - \eta_0}{\eta_0 \phi}$$

Where η_0 is the viscosity in the absence of the solute and ϕ is the volume fraction of the solute in the solution. As defined here, the intrinsic viscosity $[\eta]$ is a dimensionless number. When the solute particles are rigid spheres at infinite dilution, the intrinsic viscosity equals $\frac{5}{2}$ as shown first by Albert Einstein.

In practical settings, ϕ is usually solute mass concentration (c , g/dL), and the units of intrinsic viscosity $[\eta]$ are deciliters per gram (dL/g), otherwise known as inverse concentration. (https://en.wikipedia.org/wiki/Intrinsic_viscosity)

1.9 Osmosis:

Phenomenon of the passage of a pure solvent into a solution separate from it by semi permeable membrane. A semi permeable membrane is a membrane that is permeable to the solvent but not to the solute. The membrane might have microscopic holes that are large enough to allow water molecules to pass through, but not ions or carbohydrates molecules with their bulky coating hydrated water molecules. The Osmotic pressure π is the pressure that must be applied to the solution to stop the inward flow of solvent.

One of the most common applications of osmosis is Osmometry, the measurement of molar masses of proteins and synthetic polymers from the osmotic pressure of their solutions. as these huge molecules dissolve to produce solutions that are far from ideal (Atkines and Depaula, 2009).

The tendency of solvent molecules to pass spontaneously into a solution, due to the $\mu_1 < \mu_1^0$, is estimated quantitatively by osmotic pressure which has the dimension of pressure (atm). The π is the thermodynamic affinity between its components referred to unit volume of the solvent:

$$\pi = \frac{\Delta\mu_1}{V_1} \dots \dots \dots (1 - 1)$$

Let p° denote to the external pressure on the pure solvent, and p , pressure on the solution $p - p^\circ$ becomes equal to the osmotic pressure π

$$\pi = p - p^\circ \dots \dots \dots (1 - 2)$$

Thus, the osmotic pressure of a solution is equal to the additional pressure which must be applied to the solution to make the chemical potential of the component in solution equal to the chemical potential of the pure solvent.

The change in chemical potential of solvent with environmental pressure at constant temperature is given by equation

$$\left(\frac{\partial \mu_1}{\partial p}\right)_T = V_1' \dots \dots \dots (1 - 3)$$

$$d\mu_1 = V_1' \dots \dots \dots (1 - 4)$$

Hence

$$\int_{\mu_1}^{\mu_1^0} d\mu_1 = \int_{p^0}^p V_1' dp \dots \dots \dots (1 - 5)$$

Assuming V_1' to be constnt, we obtain after integration

$$\mu_1^0 - \mu_1 = V_1' (p - p^0) = V_1' \pi \dots \dots \dots (1 - 6)$$

Where π = osmotic pressure

V_1' = Partial specific volume of solvent.

Hence

$$\mu_1^0 - \mu_i = \Delta\mu_i = V_1' \pi \dots \dots \dots (1 - 7)$$

A comparison of equation (1-20) and (1-2) shows that the osmotic pressure of an ideal solution can be given by the relation

$$\pi = \left(-\frac{RT}{V_1^0}\right) \ln N_1 \dots \dots \dots (1 - 8)$$

In (1-N2) in a series, and using the first term of this series for high dilutions, we obtain

$$\ln N_1 = \ln(1 - N_2) = -N_2 - N_2^2/2 - \dots \dots \dots (1 - 9)$$

$$\pi (RT/V_1^0) N_2 \dots \dots \dots (1 - 10)$$

The mole fraction of a component is

$$N_2 = n_2 / (n_1 + n_2) \dots \dots \dots (1 - 11)$$

where n_1 and n_2 are the numbers of moles of the components

if $n_1 \gg n_2$ then $N_2 \approx n_2/n_1$. substiting this expression into eq (1-23) ,we

Get
$$= \pi \left(\frac{RT}{N} \right) N_2 = c_2 RT \dots \dots \dots (1 - 12)$$

Where V —volume of solution, equal to $n_1 V_1^0$

$c_2 = n_2/V =$ concentration of a solute, mole/ liter.

Equation(1-25)was first derived empirically by van't Hoff and is known as the van't Hoff equation.

The Van't Hoff equation $\pi = c_2 RT$ does not apply to polymer solutions, even though very dilute. The concentration dependence of osmotic pressure is expressed by a more complex equation if the concentration c is replaced by a power series:

$$\pi = RT(A_1 c_2 + A_2 c_2^2 + A_3 c_2^3 + \dots) \dots \dots \dots (1 - 13)$$

Or

$$\pi/c_2 = RT (A_1 + A_2 c_2 + A_3 c_2^2 \dots) \dots \dots \dots (1 - 14)$$

Where $c_2 =$ concentration of apolymer in a solution, g/ml

$A_1, A_2, A_3,$ etc. = so-called vfril coefficient, whose value can be calculated from experimental dependenc $\pi /c_2 = f(c_2)$.

In the general case this dependence is represented by curves concave to the ordinate axis, the first viral coefficient A_1 is related directly to the molecular mass of polymer by the relation $A_1 = 1/M$. Hence in the last equation may be written in the following form:

$$\pi/c = RT/(1/M + A_2c_2 + A_3c_2^3 + \dots) \dots \dots \dots (1 - 15)$$

For a number of systems the dependence $\pi /c_2 = f (c_2)$ is a straight line in the region of high dilutions, i.e., $A_3 = 0$, and Eq. (1-28) becomes simpler

$$\pi/C_2 = RT (1/M + A_2C_2) \dots \dots \dots (1 - 16)$$

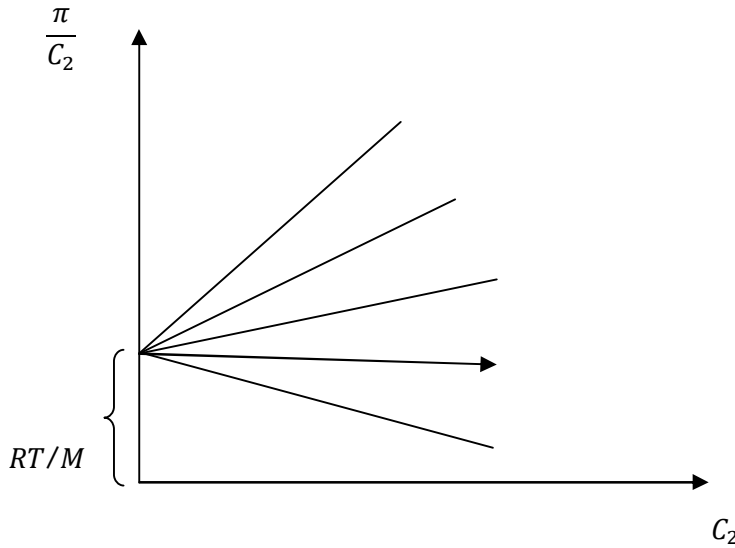


Figure (1-1): Dependence of π/c_2 on concentration for polymer solution in various solvent.

1.10 Mark–Houwink equation:

The **Mark–Houwink equation**, also known as the **Mark–Houwink–Sakurada equation** or the **Kuhn–Mark–Houwink–Sakurada equation** gives a relation between intrinsic viscosity $[\eta]$ and molecular weight M:

$$[\eta] = KM^a$$

From this equation the molecular weight of a polymer can be determined from data on the intrinsic viscosity and vice versa.

The values of the Mark–Houwink parameters, a and K , depend on the particular polymer-solvent system. For solvents, a value of $a=0.5$ is indicative of a theta solvent. A value of $a=0.8$ is typical for good solvents. For most flexible polymers, $0.5 \leq a \leq 0.8$. For semi-flexible polymers, $a \geq 0.8$. For polymers with an absolute rigid rod, such as Tobacco mosaic virus, $a = 2.0$.

1.10.1 Applications:

In size-exclusion chromatography, such as gel permeation chromatography, the intrinsic viscosity of a polymer is directly related to the elution volume of the polymer. Therefore, by running several monodisperse samples of polymer in a gel permeation chromatograph (GPC), the values of K and a can be determined graphically using a line of best fit. Then the molecular weight and intrinsic viscosity relationship is defined.

Also, the molecular weights of two different polymers in a particular solvent can be related using the Mark–Houwink equation when the polymer-solvent systems have the same intrinsic viscosity:

$$k_1 M_1^{1+a_1} = k_2 M_2^{1+a_2}$$

Knowing the Mark–Houwink parameters and the molecular weight of one of the polymers allows one to find the molecular weight of the other polymer using a GPC. The GPC sorts the polymer chains by volume and as intrinsic viscosity is related to the volume of the polymer chain, the GPC data is the same for the two different polymers. For example, if the GPC calibration curve is known for polystyrene in toluene, polyethylene in toluene can be run in a GPC and the molecular weight of polyethylene can be found according to the polystyrene calibration curve via the above equation.

1.11 Objective:

This project aims to:

- Determination of Mark–Houwink parameters for gum produced by Dr. El Fatih (polyacatha).

2. Materials and Method:

2.1 Materials:

2.1.1 Sample collection and treatment:

Polyacantha gum sample was collected by Dr. Elfatih Ahmed Hassan.

Purification and preparation sample Polyacantha gum sample used for the studies were purified from impurities such as bark, sand and dust by hand they kept in alabeled container for use.

2.1.2 Chemical:

- Acetone.
- Distilled water.

2.2 Methods:

2.2.1 Fractionation of Polyacantha gum:

About 7g of Polyacantha gum sample dissolved in 21 ml distilled water to have clear solution few drop of acetone added until a slight the solution separated into tow layers one liquid and other precipitated solid, and repeated this step in three times. .

2.2.2 Estimation average molecular weights:

Three molecular weights were obtained by using acetone and were found to be $M_1 = 9050 \text{ g/mole}$, $M_2 = 3382 \text{ g/mole}$, $M_3 = 2578.997 \text{ g/mole}$

2.2.3 Determination of intrinsic viscosity:

Three intrinsic viscosity values were obtained by making less concentration was prepared for Estimation average molecular weight and were found $[\eta]_1 = 20.88$, $[\eta]_2 = 33.2$ and $[\eta]_3 = 10.13$.

Table (3-2): variation of osmotic pressure with concentration for fraction (2):

C	π	π/C
0.06	0.88	14.66667
0.08	1.25	15.625
0.1	1.85	18.5
0.12	2.95	24.58333

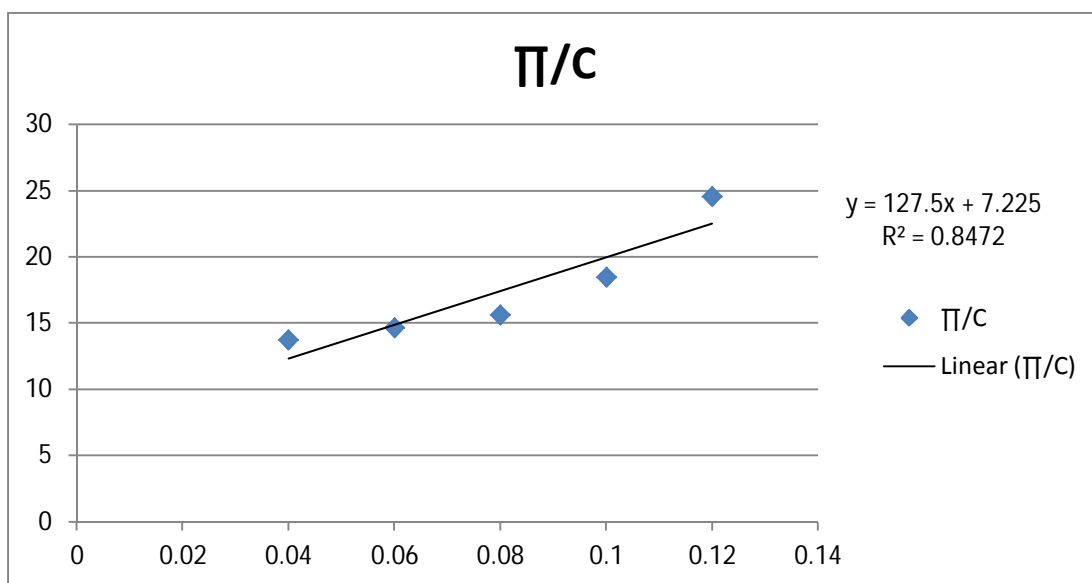


Figure (3-2): variation of π/c with c for fraction (2)

$$MWT = RT / \pi/C$$

$$0.082 * 298 / 7.225$$

$$3382.1453$$

g/mole

Table (3-3): variation of osmotic pressure with concentration for fraction (3):

C	π	π/C
0.04	0.6	15
0.06	1	16.66667
0.08	1.55	19.375
0.1	2.2	22
0.12	3	25

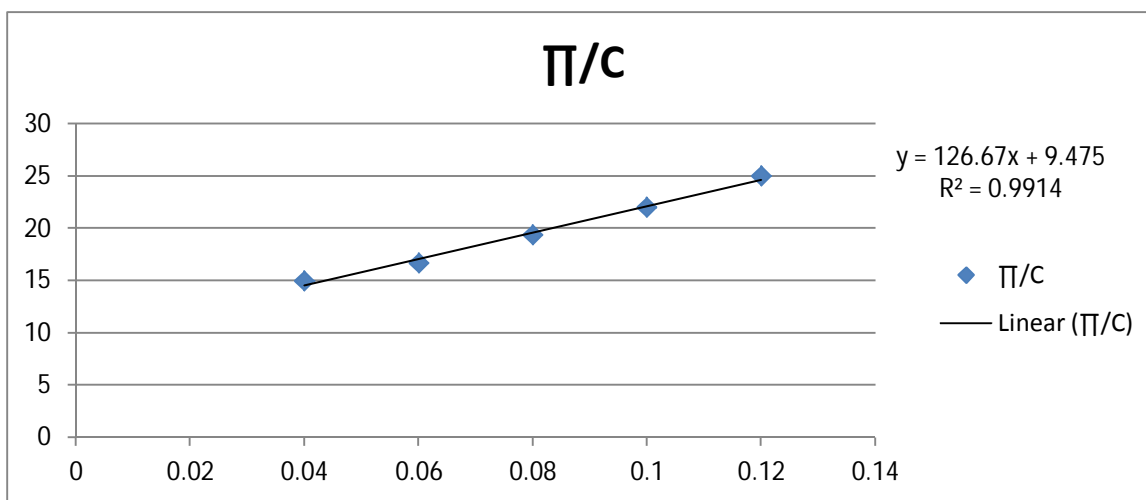


Figure (3-3): variation of π/c with c for fraction (3)

$$M = \frac{RT}{\pi/C} = \frac{0.082 \cdot 298}{9.475} = 2578.997 \text{ g/mole}$$

R=0.082
T=298

Table (3-4): variation of reduced viscosity with concentration for Fraction (1):

C	Tsec	t0	$\eta_{re}=T/t_0$	$\eta_{sp}=\eta_{re}-1$	η_{red}
0.005	1320	905	1.458564	0.45856354	91.71271
0.0025	1027	905	1.134807	0.13480663	53.92265
0.00125	950	905	1.049724	0.04972376	39.77901

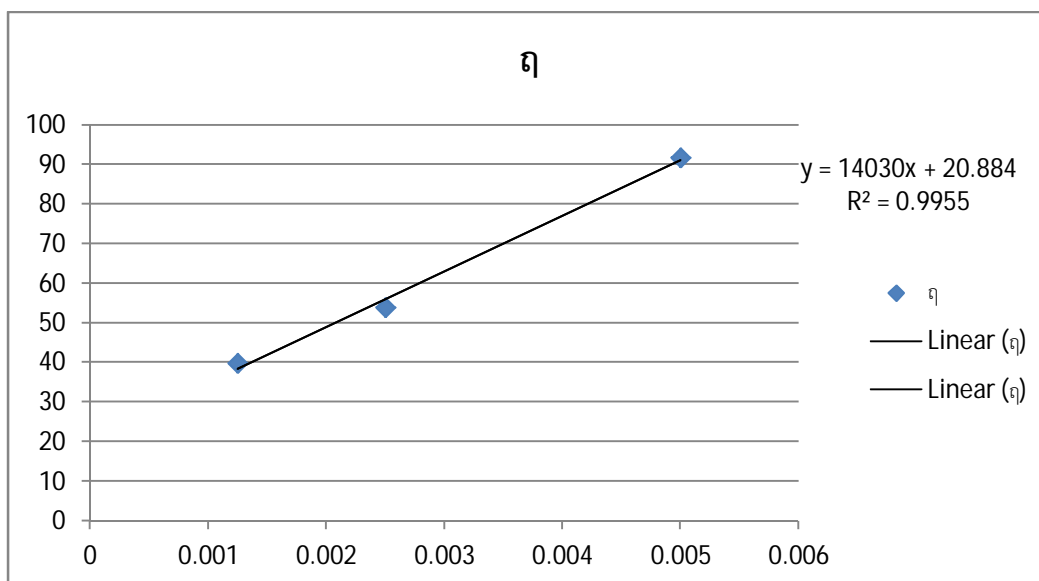


Figure (3-4): variation of η_{red} with C for fraction (1)

$$\eta = 20.88$$

Table (3-5): variation of reduced viscosity with concentration for Fraction (2):

C	Tsec	t ₀	$\eta_{re}=T/t_0$	$\eta_{sp}=\eta_{re}-1$	η_{red}
0.005	1214	950	1.227	0.277	55.4
0.0025	1040	950	1.094	0.094	37.6
0.00125	1000	950	1.052632	0.052632	42.1

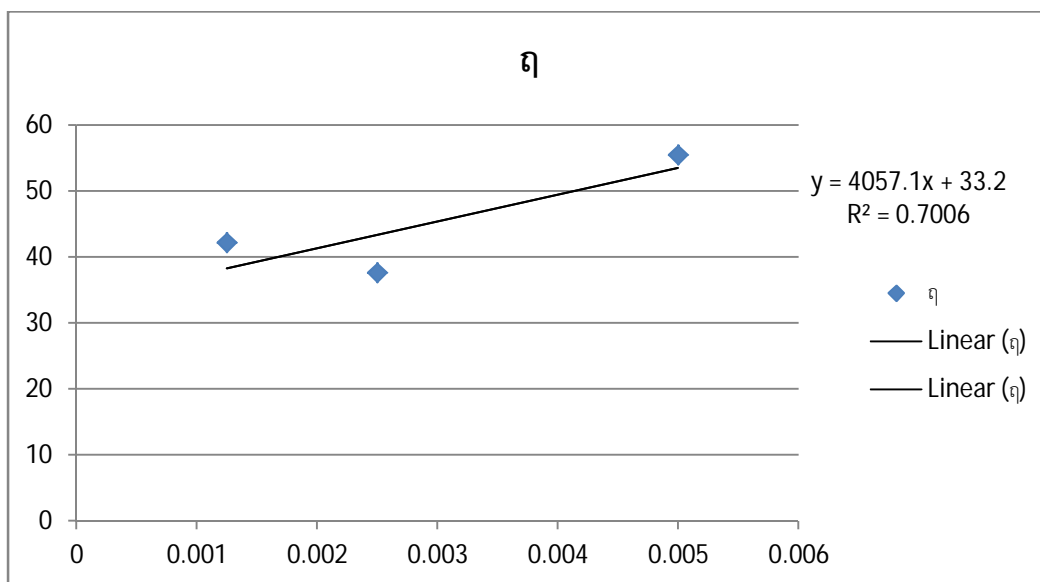


Figure (3-5): variation of η_{red} with C for fraction (2)

$$[\eta]=33.2$$

Table (3-6) variation of reduced viscosity with concentration for Fraction (3):

C	Tsec	t0	$\eta_{re}=T/t_0$	$\eta_{sp}=\eta_{re}-1$	η_{red}
0.005	1018	950	1.075	0.075	24
0.0025	988	950	1.04	0.04	16
0.00125	978	950	1.03	0.03	14.13

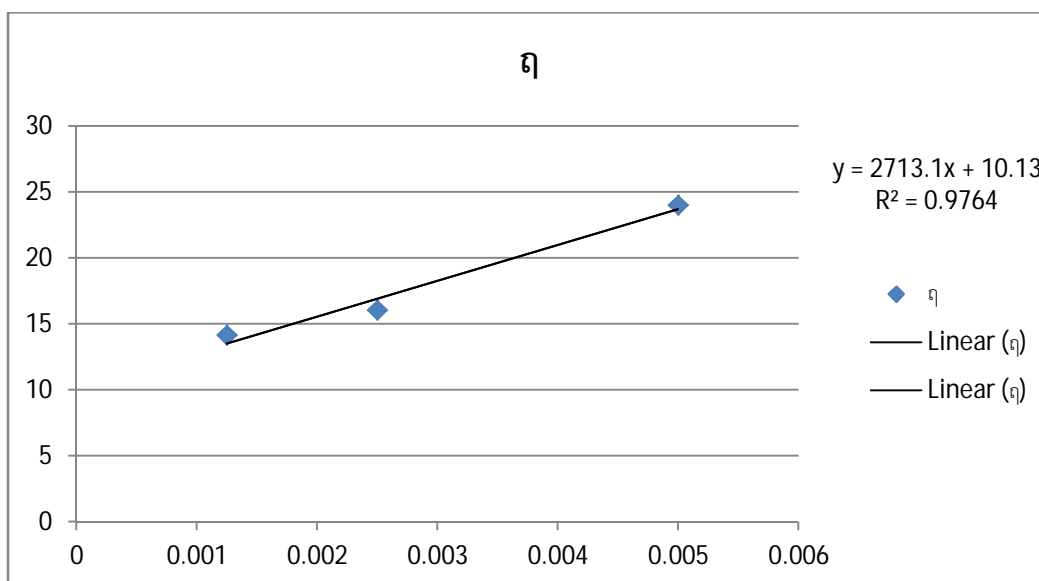


Figure (3-6): variation of η_{red} with C for fraction (3)

$[\eta] = 10.13$

Table (3-7): variation of logarithm different molecular weight with logarithm different intrinsic viscosity:

M	[η]	Log M	Log [η]
9050	20.884	3.9566	1.3198
3382	33.2	3.529	1.5211
2578	10.13	3.4114	1.0056

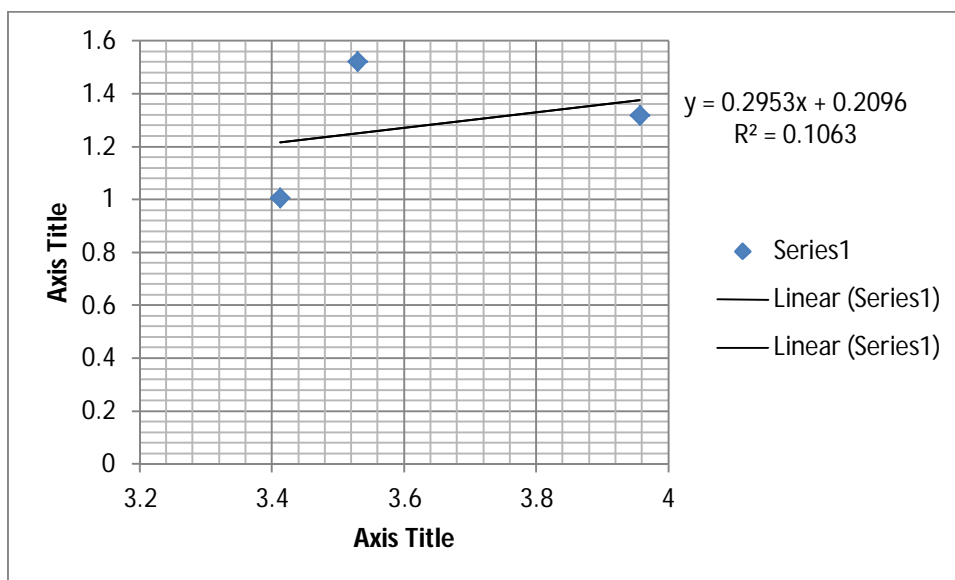


Figure (3-7): Variation \bar{M}_n with logarithm [η]

Log K= intercept = 0.209

$\alpha = slop \simeq 0.3$

Anti log = 1.2324

K=1.234

3.2 Discussion:

From obtained result were found the values of viscosity, $[\eta]_1 = 20.884$, $[\eta]_2 = 33.2$ and $[\eta]_3 = 10.13$ for fraction 1.2.3 respectively and values of average molecular weighs were found $M_1 = 9050$, $M_2 = 3382.1453$ and $M_3 = 2578.997$ for fraction 1.2.3 respectively and values of logarithm of each average molecular and were obtained $\log M_1 = 3.9566$, $\log M_2 = 3.529$ and $\log M_3 = 3.4114$ for fraction 1.2.3. respectively finally were plotting logarithm average molecular weigh with logarithm intrinsic viscosity to obtained Mark-Houwnink parameters and were found $K = 1.2324$ and $\alpha \simeq 0.3$.

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