Chapter 2

Effect of initiator and inhibitor on the molecular weight of poly (acrylic acid)

2.1 Introduction

Various commercially useful polymers are selected on the basis of their properties such as melt viscosity, impact strength or tensile strength. These properties are directly dependent on the molecular weight of the polymer or its degree of polymerization[1]. At very high molecular weights, the melt viscosity rises more steeply than at low molecular weights. A commercially useful polymer should have a low melt viscosity to permit ease of processing, but, at the same time, should exhibit good strength. The effectiveness study of the relatively low molecular weight poly(acrylic acid) (i.e. PAA) shows that the chains most linear and atactic polymers, devoid of secondary and tertiary structures, tend to fold within each other to form a mass of interpenetrating random coils, not unlike a bowl of spaghetti[2], and this tendency increases as the polymer size increases. The polymeric chains tend to unfold in solution but the extent of this unfolding is a function of the nature of the solvent and the temperature. Under Ѳ conditions, that is the Ѳ solvent and the Flory temperature, an optimal unfolding result and the chains are more opened and disentangled[3]. In addition to the natural folding of linear polymeric chains of PAA, there are the folding due to the hydrogen bonding between the carboxylic groups either intermolecularly or intramolecularly. To recall, the theta solvent and temperature for PAA are dioxane and 30^{o}C, respectively[4]. However, in our working conditions, the longer PAA chains are folded to a certain degree and the carboxylic functions are not all exposed. Most of them are embedded in the core, and consequently, the sequestration of the metallic ions, by the carboxylic groups is not quantitative. In the case of shorter PAA chains, the unfolding is more accessible and prone to the complexation with metallic ions. PAA is produced in large quantities for industrial materials such as dispersants, thickeners and super absorbent polymer[5-10]. In particular, cross-linked PAA absorbs a large number of water and is used in humidity control and baby diapers. PAA is produced by radical polymerization in heterogeneous systems (inverse suspension[11,12]/ miniemulsion polymerizations[13]) as particle state as well as homogeneous system (solution polymerization). However, in the case of the heterogeneous systems, large amounts of volatile organic compounds are employed because PAA is water-soluble.

According to the literature, poly (acrylic acid) is quite versatile in many applications, particularly in the removal of heavy and radioactive metallic ions, and new applications are ever increasing[14]. Doherty et al has reported a study of the inhibition of calcium oxalate using poly (acrylic acid)[15]. This thesis is focused on the effects of the molecular weight of the antiscalants rather than the chemical components. The role and tendencies of the molecular weight (MW) of PAA antiscalants is somewhat unclear seeing as studies typically use free-radical polymerized PAAs[16-18].

Scale is the precipitate that forms on surfaces in contact with water as a result of the precipitation of normally soluble solids that become insoluble as temperature increases. Some examples of scale are calcium carbonate, calcium sulphate, and calcium silicate.

Scale inhibitors are surface-active negatively charged polymers. Such as calcium carbonate scale reduces process efficiency and control in kraft pulping operations. As minerals exceed their solubility's and begin to merge, the polymers become attached. The structure for crystallization is disrupted and the formation of scale is prevented. The particles of scale combined with the inhibitor will than be dispersed and remain in suspension.

The formation of scale can be alleviated or at least reduced by the addition of antiscalant chemicals into the process line. A number of different antiscalants are commercially available but still little is known about their mechanism of inhibiting scale formation. Examples of scale inhibitors are phosphate esters, phosphoric acid and solutions of low molecular weight polyacrylic acid. This chapter focuses on one class of antiscalants, the polymeric antiscalants, which are carboxylic acid containing polymers. Scale inhibition performance at high pH and temperatures was characterized using a number of different experimental setups and the mechanisms involved were investigated[19-37]. The most influential characteristic of the polymeric antiscalants was the molecular weight (MW), and consequently, the molecular weight distribution (MWD) of the polymer species. Acrylic acid is used as the base (and majority) monomer in almost all commercial polymeric antiscalants. Since commercial poly (acrylic acid) (PAA) samples have a broad MWD. PAA prepared by free-radical polymerization has a broad molecular weight distribution. In addition, specific MW effects on inhibition mechanisms such as morphology modification and adsorption tend to be reported and discussed at most as secondary interests[38] with MW distribution effects being completely ignored. As far as general antiscalant behavior goes, results have been reported suggesting a general optimal MW range being less than 20,000 g/mol but dependant upon antiscalant structure, inhibited salt, and reaction conditions. The information presented here is useful both in identifying important properties of polymeric antiscalants and in understanding the mechanisms by which they inhibit the formation of calcium carbonate crystalline deposits in kraft pulping.

The various phases of scale formation, beginning with a supersaturated solution and moving through nucleation and crystal growth to end with deposited scale surfaces and the schematic representations of how antiscalants can prevent the system from progressing forward towards deposition noting that the methods involved in scale inhibition are determined by a number of things such as pH, temperature, and concentrations (of antiscalant and the slightly soluble components) has been shown in Fig. 2.1.

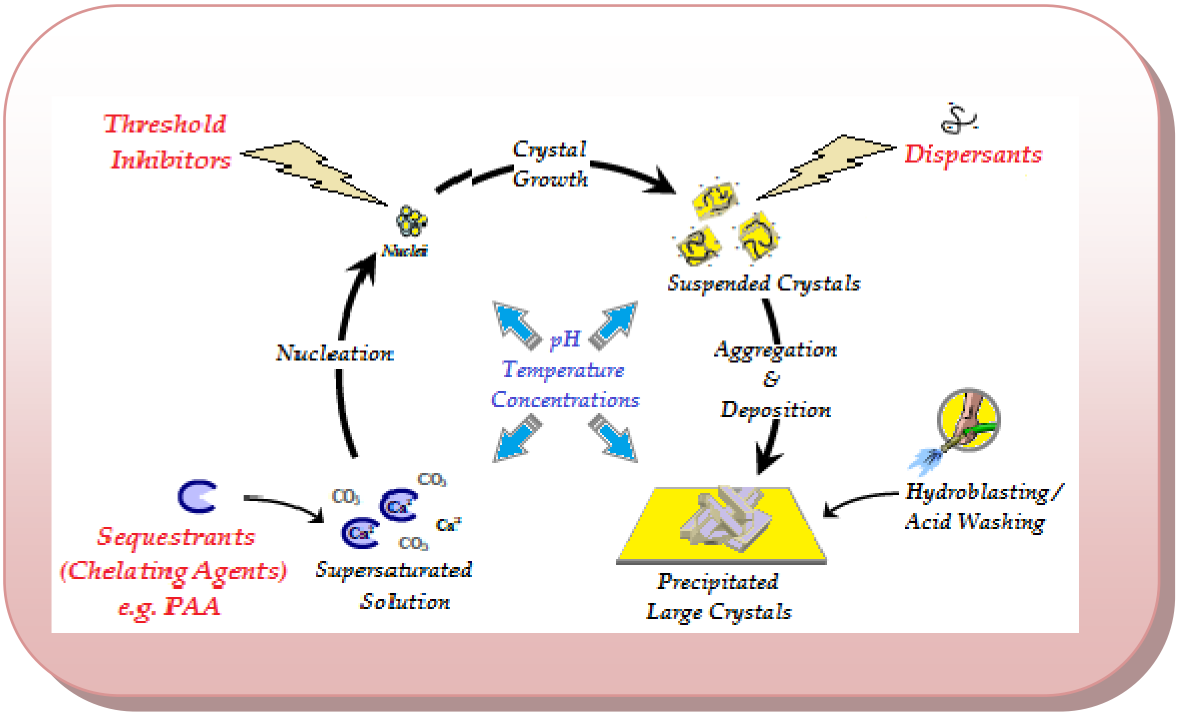


Figure 2.1 *A schematic outline depicting the various phases of scale formation*

The polymerization technique has been used here was solution polymerization which implied the use of water as a solvent which enhanced to control viscosity of reaction mixture. During termination step to control the molecular weight the growing polymer chain, i.e. also called initiating radicals, need to be terminated at different small chain lengths because in case of polymers the molecular weight is calculated as a average of molecular weight of all polymer molecule chain. Other mechanisms that can affect this process include the inhibition or retardation of free radical initiation, chain transfer of the radical center to other molecules in the reaction medium, and branching reactions[39-41].

Inhibitors (e.g. allyl alcohol, allyl chloride, hydroquinone etc.) and retarders react with initiating and propagating radicals and convert them to non-radical species or radicals with low reactivity[42]. Inhibitors stop every radical they encounter, and polymerization is completely halted until they are consumed. Retarders are less efficient and only stop a portion of the radicals[43]. Many free radical reactions exhibit an induction period, during which inhibitors and retarders are reacted away[44]. Mechanism for Inhibitors during polymerization:

Decomposition: $I \longrightarrow 2R^{\bullet}$

Initiation: $M + R^{\bullet} \longrightarrow R{-}M^{\bullet}$

Propagation: $M_n^{\bullet} + M \longrightarrow M_{n+1}^{\bullet}$

Termination: $\underset{\text{Growing chain}}{M_n^{\bullet}} + \underset{\text{Inhibitor}}{XA} \longrightarrow M_n{-}X + A^{\bullet}$

Where if $A^{\cdot}$ is a unreactive radical then XA is an inhibitors, otherwise if $A^{\bullet}$ reinitiates the reaction then XA is a chain transfer agent[45, 46]. The inhibitors used were:

1) Allyl chloride $\Longrightarrow$ $CH_2{=}CH{-}CH_2{-}Cl$

2) Allyl alcohol $\Longrightarrow$ $CH_2{=}CH{-}CH_2{-}OH$

So, this chapter focuses on the synthesis of low molecular weight poly (acrylic acid) via. variation in concentration of initiators and inhibitors during polymerization of acrylic acid. It is done by using free-radical polymerization method with solution polymerization technique. The synthesized polymers were then characterized by FT-IR and the molecular weight determination was done by viscosity average method. Later its metal sequestration ability was also determined by titration method.

2.2 Experimental

2.2.1 Materials

Acrylic acid monomer was purchased from Merck and purified by passing through alumina column and subsequent drying under molecular sieves[47]. Hydrogen-peroxide and L-ascorbic acid, allyl alcohol, allyl chloride and 1, 4-dioxane were purchased from Merck and used as received.

2.2.2 Instruments and Measurements

FT-IR spectroscopic measurements were recorded on a Shimadzu 8400S Fourier Transform Infrared Spectrometer by KBr pellet method.

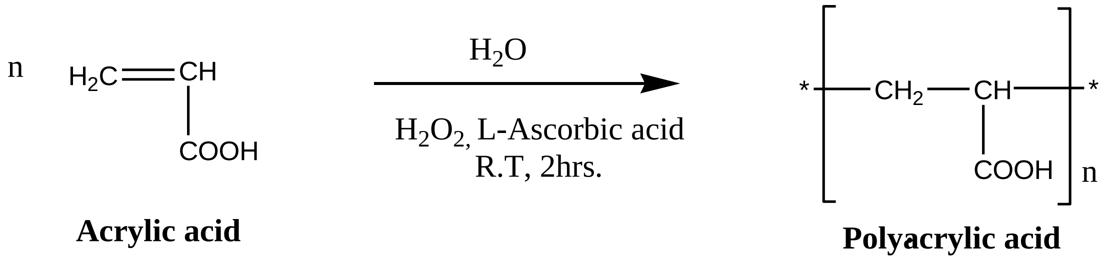
Molecular weights of the PAA's were determined by viscosity average method with 1, 4-dioxane as a solvent having 'k' and 'a' constants 76×10^{-3} & 0.5 are respectively[48]. Its metallic sequestration capability was also studied by titration method[49].

2.2.3 Synthesis

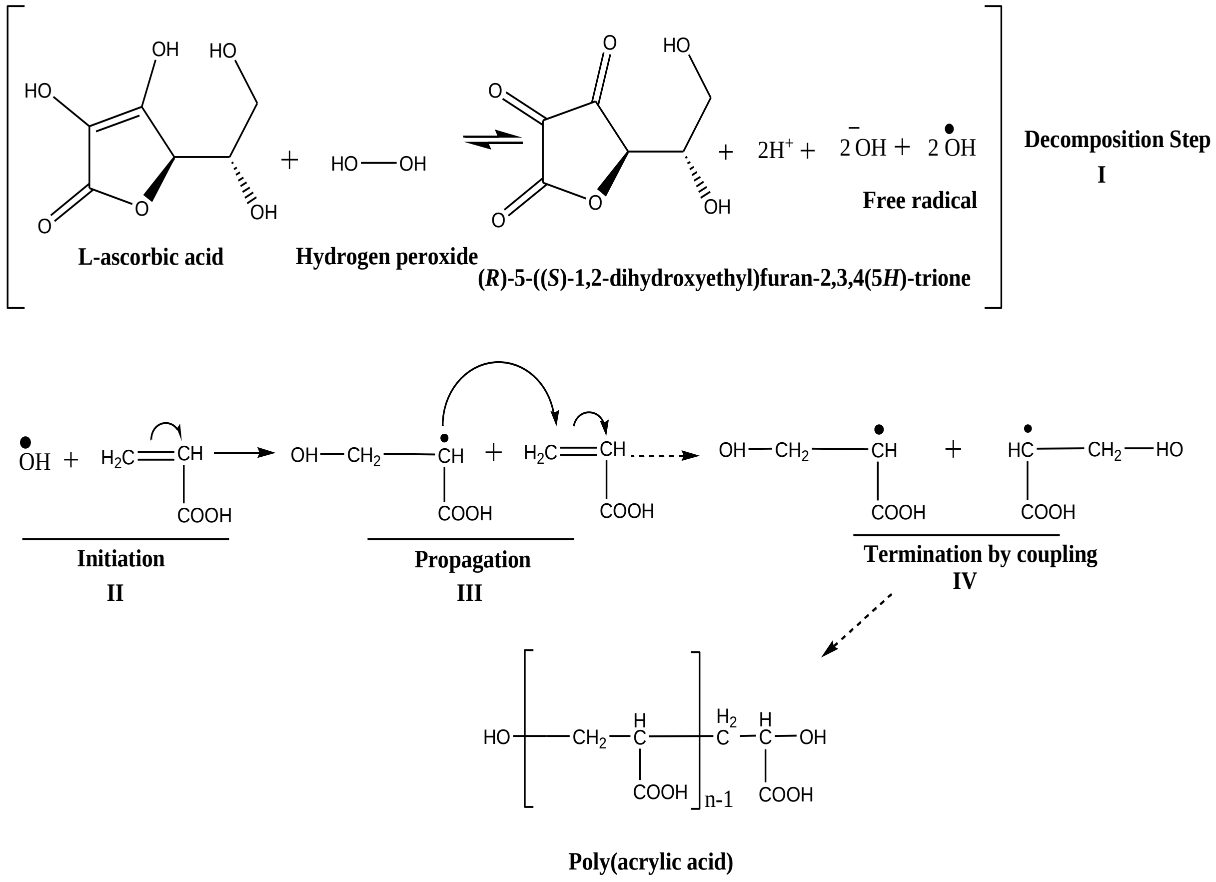
(A) Synthesis of PAA by varying concentration of initiators

Scheme 2.1 consist the procedure used for the synthesis of poly (acrylic acid). A certain amount of L-ascorbic acid (weight % of monomer) was separately dissolved in 100 ml of water as a solvent was taken in a three-neck reactor equipped with nitrogen purging with continuous stirring. At room temperature simultaneously 20 ml of acrylic acid and initiator, 30% hydrogen peroxide (weight % of monomer), were added dropwise. So due to the exothermic reaction temperature of the reaction raised, so stirring continued till the temperature of the solution comes to room temperature and a viscous solution was obtained which was then diluted with distilled water and ultra filtered through 650Da molecular weight cutoff membrane. Then this solution was freeze dried in contrast to conventional method, i.e. directly vaccum dried the viscous-solution to white fluffy solid material. Then it was characterized by FT-IR and the molecular weight was determined through viscosity average method by using Ubbelohde viscometer.

Scheme



Mechanism

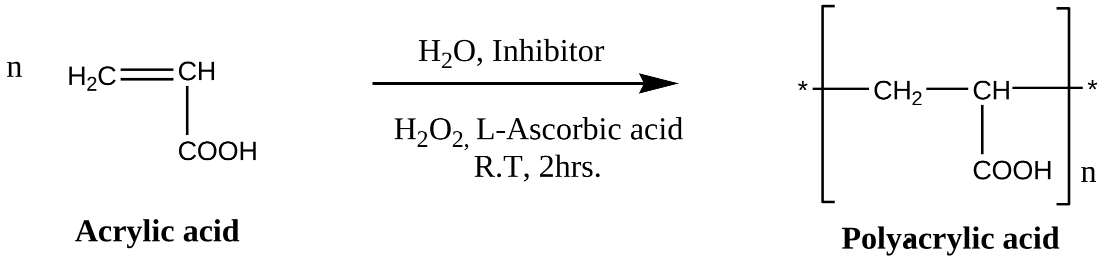


Scheme 2.1 Synthesis of poly(acrylic acid) with mechanism.

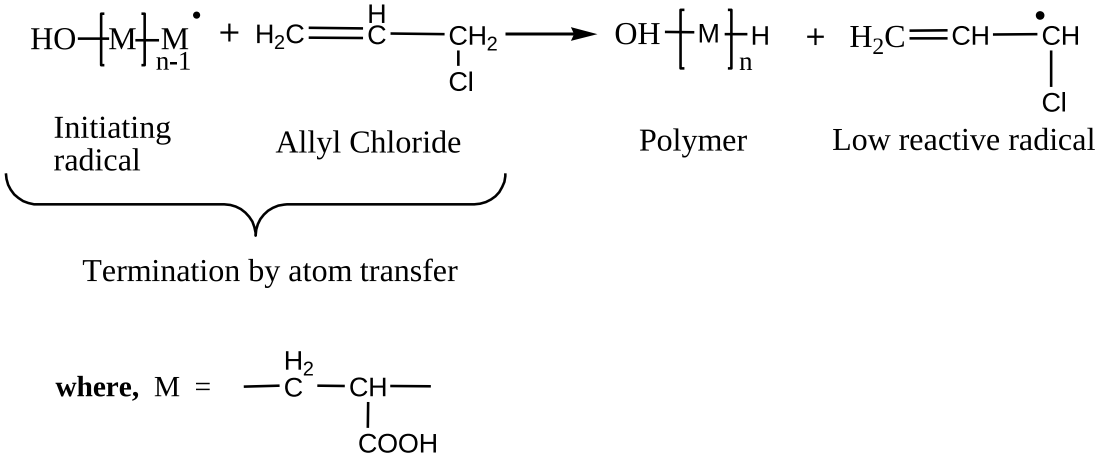
(B) Synthesis of PAA by varying concentration of inhibitors

Scheme 2.2 consist the procedure used for the synthesis of poly (acrylic acid). A certain amount of L-ascorbic acid (1% of monomer) was separately dissolved in 100 ml of water as a solvent was taken in a three-neck reactor equipped with nitrogen purging with continuous stirring. At room temperature simultaneously 20ml of acrylic acid and initiator, 30% hydrogen peroxide (1% of monomer), were added dropwise. As the exothermic reaction started addition of inhibitor were also done. Stirring continued till the temperature of solution comes to room temperature and a viscous solution was obtained which is then ultra filtered through 600Da mw cutoff membrane. Then the solution was freeze dried in contrast to conventional method, i.e. directly vaccum dried the viscous solution, then a white fluffy solid was obtained which is characterized by FT-IR. Similar procedure was followed for the synthesis of all samples of PAA. Then these samples were characterized for their metal sequestration property and molecular weight determination as in section A.

Scheme



Mechanism



Scheme 2.2 Synthesis of poly(acrylic acid) by using inhibitor with mechanism

2.2.4 Determination of metallic sequestration capability of PAAs

2.5g of PAA polymer sample was dissolved in 100ml of water. Then 10ml of 2% Na_2CO_3 was added to above solution and pH was adjusted to 11 by adding 1N NaOH. Then above solution was titrated against 0.25N calcium acetate solution till slight turbidity. The calculation of sequestration of synthesized polymer sample, shown in Table 1, was done by using a formula

$$\text{CaCO}_3\text{ (mg) sequestrated by per gram of polymer} = \frac{\text{Volume of Ca (CH}_3\text{ COO)}_2\text{ . A}}{\text{B}} \times 100$$

Where A and B are normality of calcium acetate and weight of polymer sample respectively.

2.3 Result & discussion

2.3.1 FT-IR Spectra

Fig. 2.2 consist the FT-IR spectra of synthesized poly (acrylic acid). The conversion of acrylic acid to its polymer was confirmed by the absence of C=C bond in poly (acrylic acid) spectra which usually comes around 1630-1680 cm^{-1}.

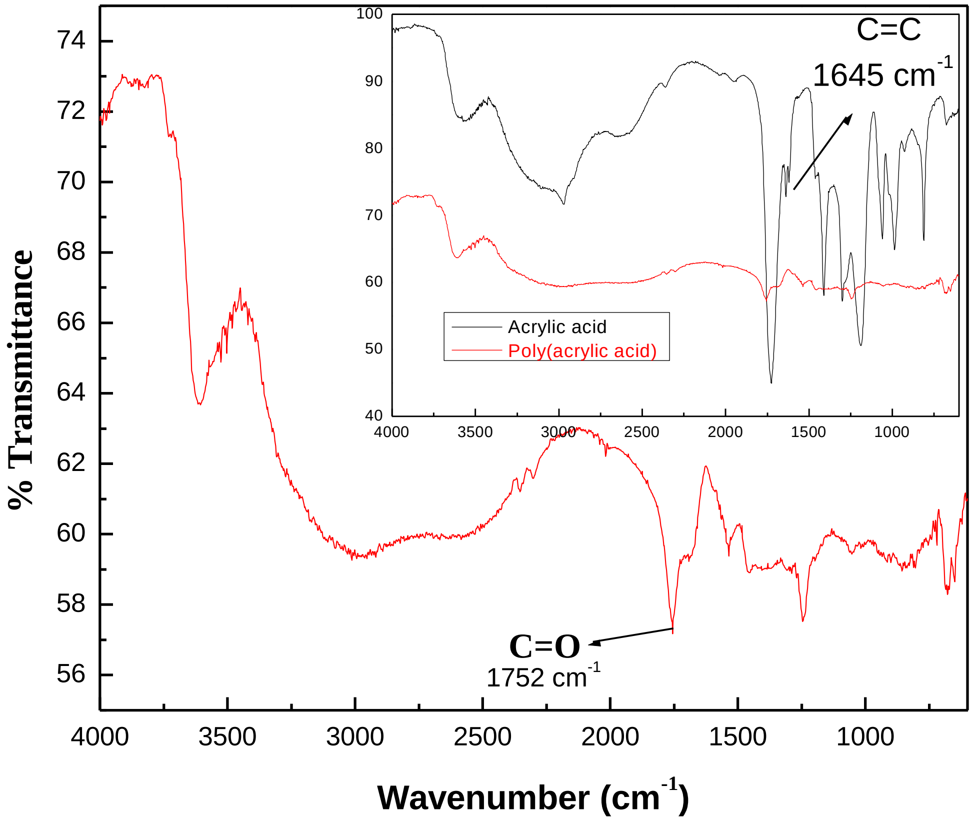


Figure 2.2 FT-IR spectra of PAA

2.3.2 Viscosity-average method

The molecular weight of synthesized polymers (shown in Table 2.17, 2.18 and 2.19) was analyzed by using Ubbelohde viscometer (Fig. 2.3). It is done by preparing different concentrations of polymer sample in a solvent, i.e., 1, 4-dioxane having particular ‘k’ and ‘a’ constants value 76×10^{-3} & 0.5 are respectively for PAA, and by recording the flow time period in seconds for these prepared polymer solutions from A (upper meniscus) to B (lower meniscus) as shown in Fig. 2.3. Later obtained viscosity data was plotted for computing intrinsic viscosity [η]. Then by using this intrinsic viscosity value in Mark-Houwink equation, as given below, the molecular weight can be calculated.

$$[\eta] = K\, Mw^{a}$$

$$Mw = ([\eta] / K)^{1/a}$$

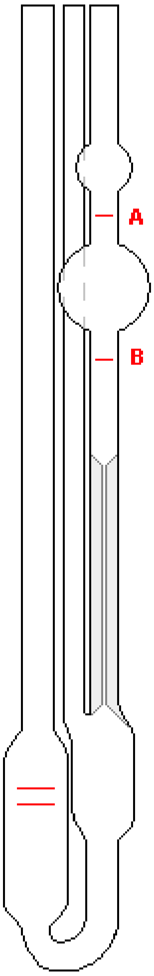


Figure 2.3 Ubbelohde Viscometer

(A) Viscosity Plot for PAA Samples from variation in concentration of initiator :

1. PAA-I **Table 2.1** Viscosity data for a PAA-I in 1, 4-dioxane solution at RT

Sr. No.	Conc. (g/dl)	Time t(sec)	η_r =t/to	η_{sp} =η_r- 1	η_{sp}/C	ln(η_r)/C
1	1,4-dioxane	t_o= 110.18	-	-	-	-
2	0.01	119.85	1.0878	0.0878	8.7888	8.4238
3	0.008	117.82	1.0693	0.0693	8.6674	8.3801
4	0.006	115.86	1.0515	0.0515	8.5981	8.3836
5	0.004	113.93	1.0340	0.0340	8.5011	8.3597
6	0.002	112.04	1.0169	0.0169	8.4532	8.3793

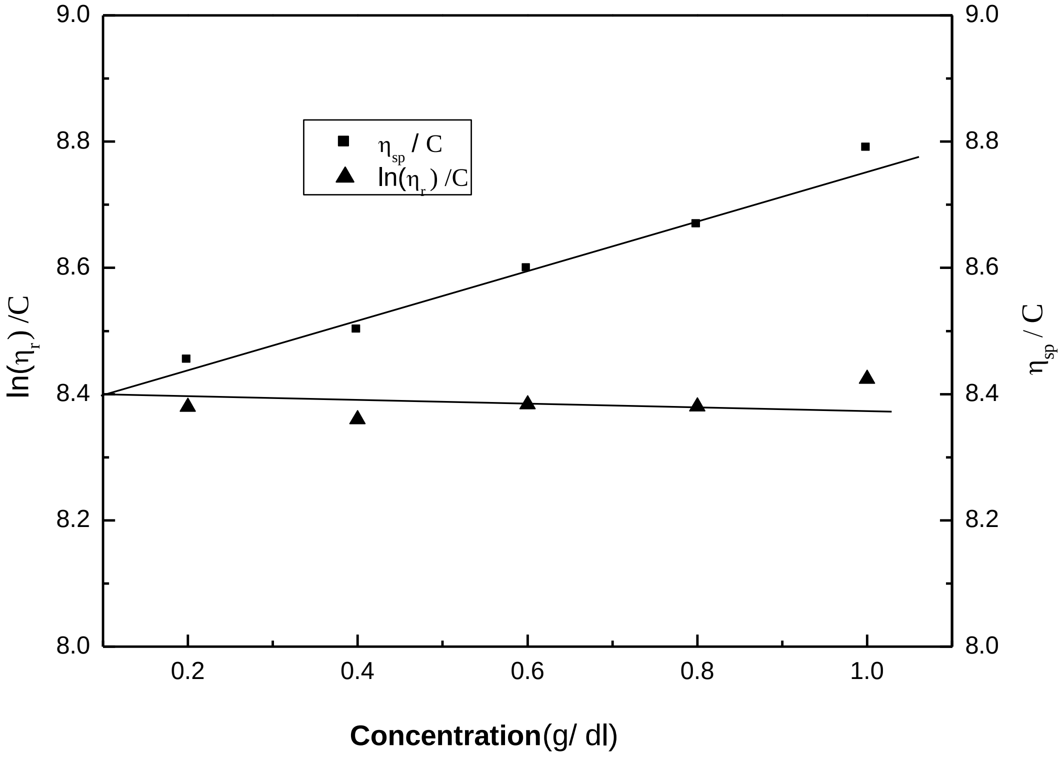


Figure 2.4 Plot for viscosity data for computing intrinsic viscosity [η] for PAA-I

Mark-Houwink equation:

$$[\eta] = K\,Mw^{a}$$

$$Mw = ([\eta] / K)^{1/a}$$

Calculation:

$$Mw = [8.4008/76x10^{-3}]^{1/0.5}$$

$$= 12{,}218.4 \text{ gm/mol}$$

2. PAA-II

Table 1.2 Viscosity data for a PAA-II in 1, 4-dioxane solution at RT

Sr. No.	Conc. (g/dl)	Time t(sec)	η_r =t/to	η_{sp} =η_r- 1	η_{sp}/C	ln(η_r)/C
1	1,4-dioxane	t_o= 110.18	-	-	-	-
2	0.01	119.49	1.0845	0.0845	8.4522	8.1119
3	0.008	117.55	1.0669	0.0669	8.3696	8.0946
4	0.006	115.48	1.0481	0.0481	8.0253	7.8380
5	0.004	113.55	1.0306	0.0306	7.6712	7.5558
6	0.002	111.81	1.0148	0.0148	7.4378	7.3830

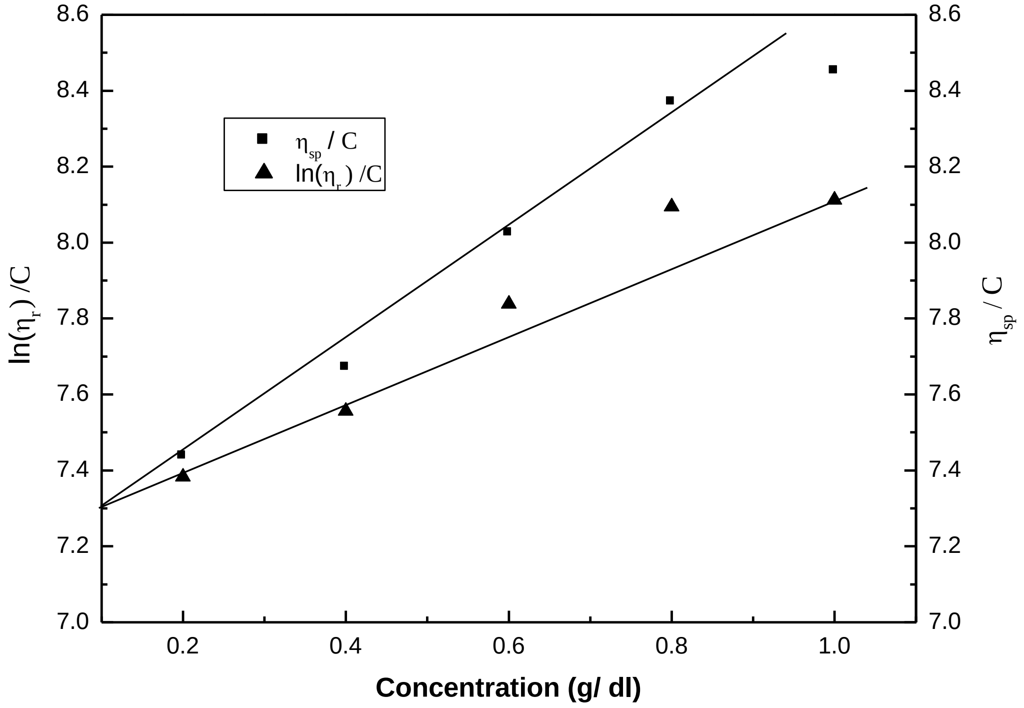


Figure 2.5 Plot for viscosity data for computing intrinsic viscosity [η] for PAA-II

Mark-Houwink equation :

$$[\eta] = K\ Mw^{a}$$

$$Mw = ([\eta] / K)^{1/a}$$

Calculation :

$$Mw = [7.3063/76x10^{-3}]^{1/0.5}$$

$$= 9242.04\ gm/mol$$

3. PAA-III

Table 2.3 Viscosity data for a PAA-III in 1, 4-dioxane solution at RT

Sr. No.	Conc. (g/dl)	Time t(sec)	η_r =t/to	η_{sp} =η_r- 1	η_{sp}/C	ln(η_r)/C
1	1,4-dioxane	t_o=110.18	-	-	-	-
2	0.01	119.01	1.0801	0.0801	8.0111	7.7053
3	0.008	117.06	1.0625	0.0625	7.8167	7.5780
4	0.006	115.06	1.0443	0.0443	7.3990	7.2244
5	0.004	113.35	1.0288	0.0288	7.2109	7.0982
6	0.002	111.75	1.0143	0.0143	7.1901	7.1388

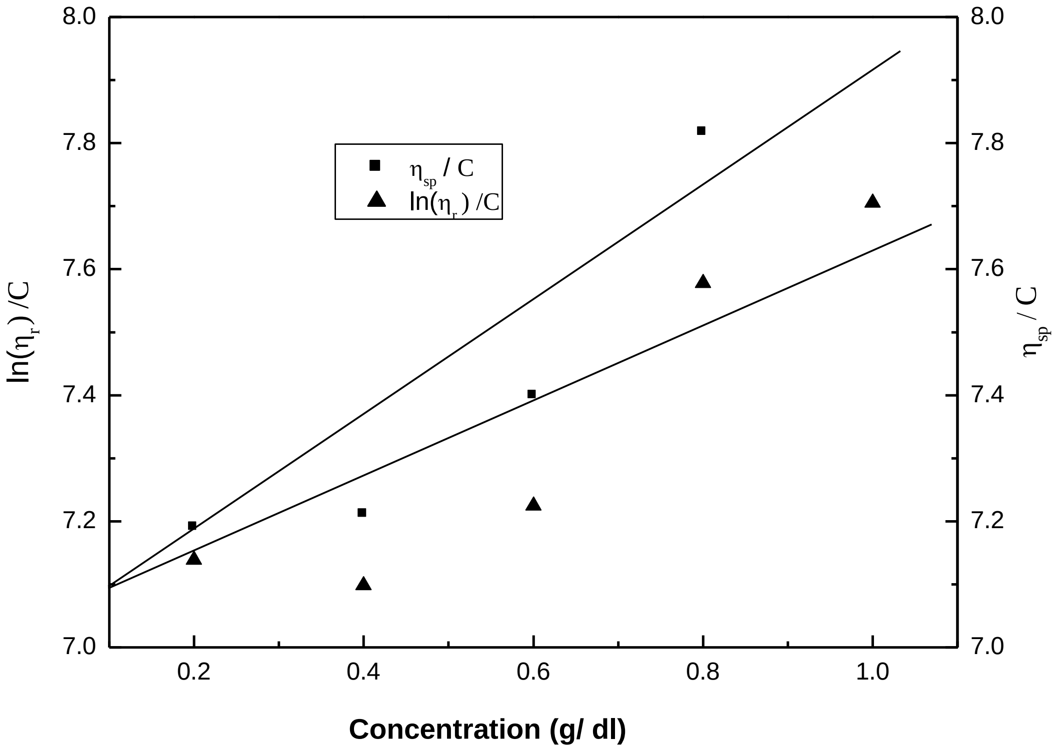


Figure 2.6 Plot for viscosity data for computing intrinsic viscosity [η] for PAA-III

Mark-Houwink equation :

$$[\eta] = K\,Mw^{a}$$

$$Mw = ([\eta] / K)^{1/a}$$

Calculation :

$$Mw = [7.1025/76\text{x}10^{-3}]^{1/0.5}$$

$$= 8733.64 \text{ gm/mol}$$

4. PAA-IV

Table 2.4 Viscosity data for a PAA-IV in 1, 4-dioxane solution at RT

Sr. No.	Conc. (g/dl)	Time t(sec)	η_r =t/to	η_{sp} =η_r- 1	η_{sp}/C	ln(η_r)/C
1	1,4-dioxane	t_o=110.18	-	-	-	-
2	0.01	118.85	1.0787	0.0787	7.8706	7.5756
3	0.008	116.85	1.0606	0.0606	7.5855	7.3543
4	0.006	115.10	1.0447	0.0447	7.4495	7.2878
5	0.004	113.32	1.0285	0.0285	7.1414	7.0413
6	0.002	111.69	1.0137	0.0137	6.8909	6.8438

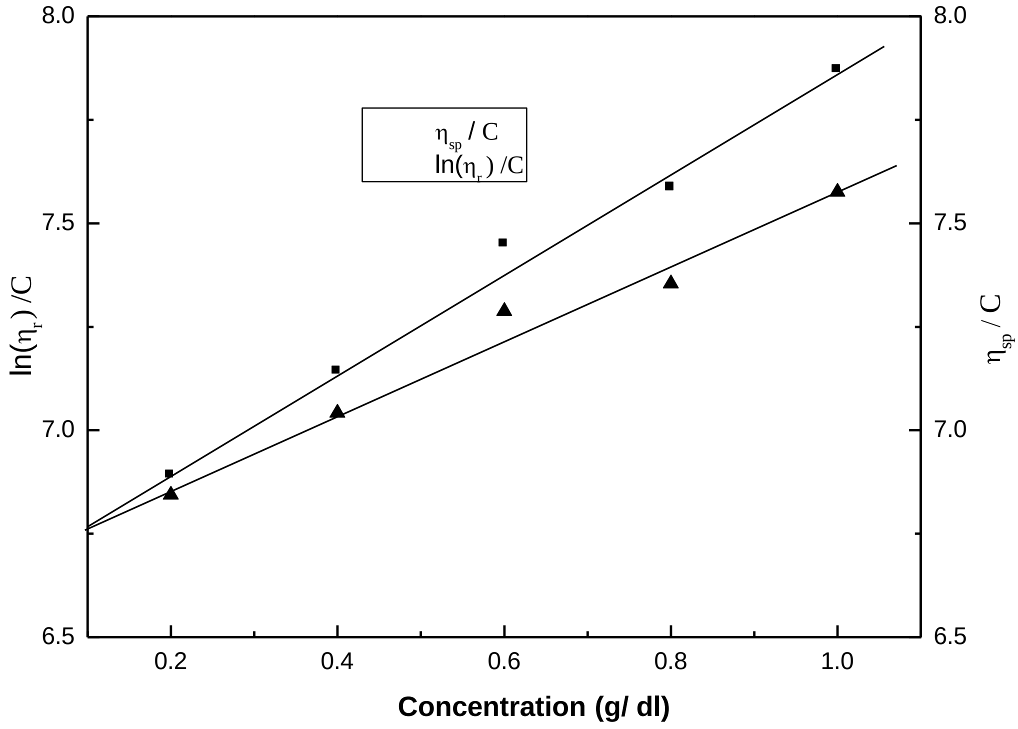


Figure 2.7 Plot for viscosity data for computing intrinsic viscosity [η] for PAA-IV

Mark-Houwink equation :

$[\eta] = K\ Mw^{a}$

$Mw = ([\eta] / K)^{1/a}$

Calculation :

$Mw = [6.7669/76x10^{-3}]^{1/0.5}$

$= 7927.8$ gm/mol

5. PAA-V

Table 2.5 Viscosity data for a PAA-V in 1, 4-dioxane solution at RT

Sr. No.	Conc. (g/dl)	Time t(sec)	$\eta_r = t/to$	$\eta_{sp} = \eta_r - 1$	η_{sp}/C	$\ln(\eta_r)/C$
1	1,4-dioxane	t_o=110.18	-	-	-	-
2	0.01	118.17	1.0725	0.0725	7.2518	6.9992
3	0.008	116.37	1.0562	0.0562	7.0333	6.8425
4	0.006	114.74	1.0414	0.0414	6.9128	6.7732
5	0.004	113.12	1.0267	0.0267	6.6698	6.5823
6	0.002	111.62	1.0131	0.0131	6.5842	6.5412

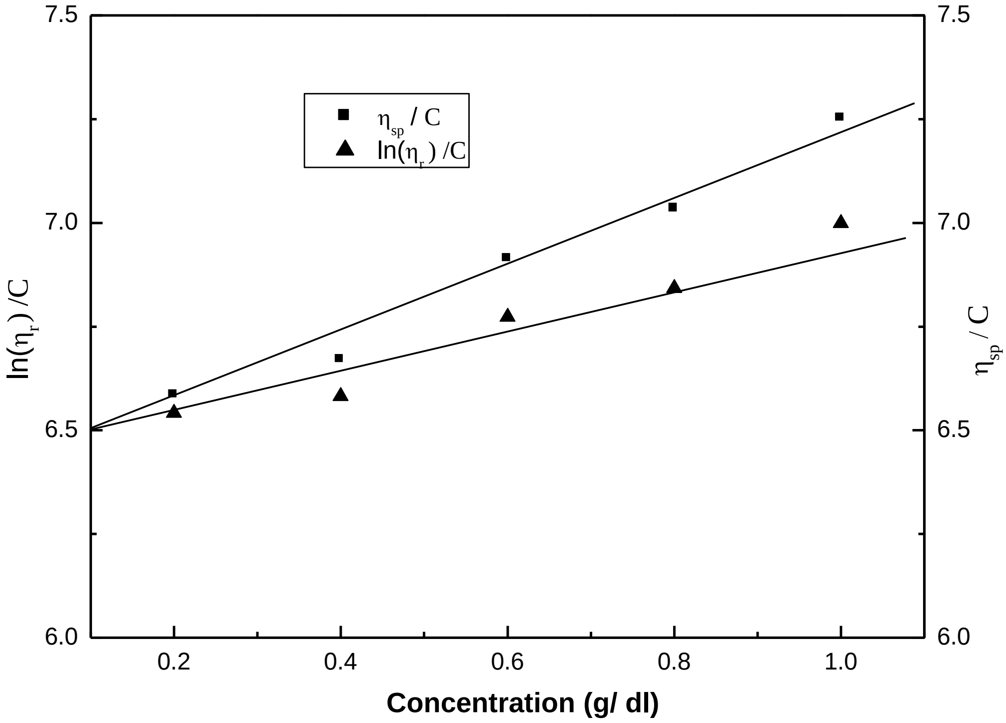


Figure 2.8 Plot for viscosity data for computing intrinsic viscosity [η] for PAA-V

Mark-Houwink equation :

$[\eta] = K\, Mw^a$

$Mw = ([\eta] / K)^{1/a}$

Calculation :

$Mw = [6.5070/76x10^{-3}]^{1/0.5}$

$= 7330.5$ gm/mol

6. PAA-VI

Table 2.6 Viscosity data for a PAA-VI in 1, 4-dioxane solution at RT

Sr. No.	Conc. (g/dl)	Time t(sec)	η_r =t/to	η_{sp} =η_r- 1	η_{sp}/C	ln(η_r)/C
1	1,4-dioxane	t_o=110.18	-	-	-	-
2	0.01	117.57	1.0671	0.0671	6.7105	6.4944
3	0.008	115.97	1.0526	0.0526	6.5786	6.4113
4	0.006	114.45	1.0388	0.0388	6.4716	6.3443
5	0.004	112.98	1.0254	0.0254	6.3531	6.2737
6	0.002	111.56	1.0125	0.0125	6.2594	6.2205

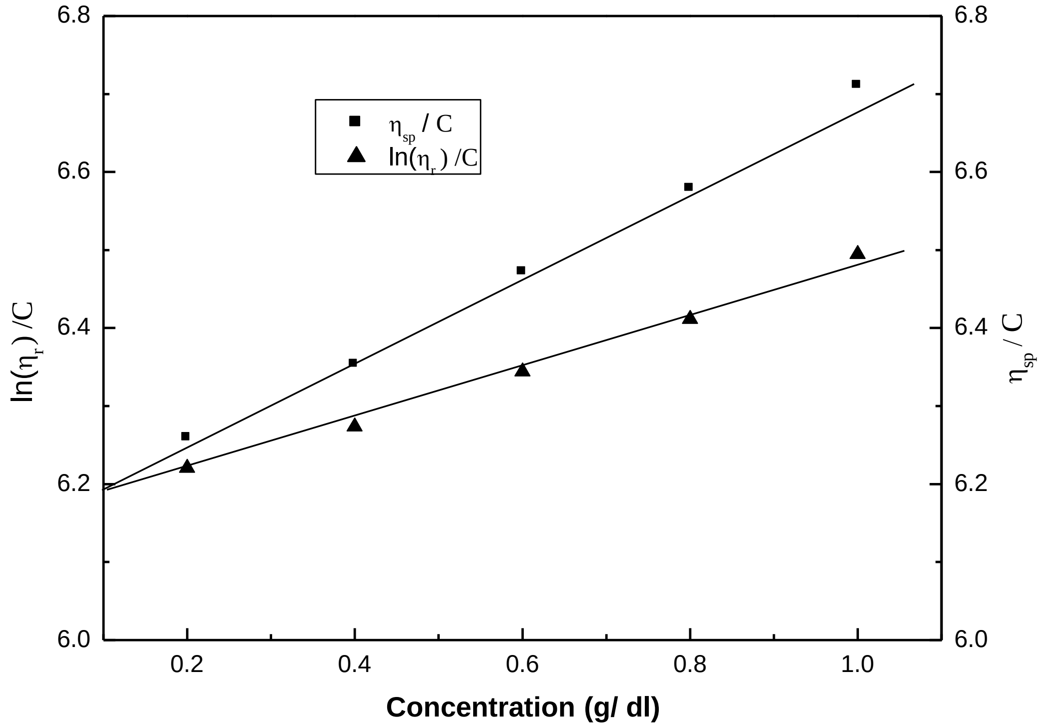


Figure 2.9 Plot for viscosity data for computing intrinsic viscosity [η] for PAA-VI

Mark-Houwink equation :

$[\eta] = K\, Mw^{a}$

$Mw = ([\eta] / K)^{1/a}$

Calculation :

$Mw = [6.1922/76\text{x}10^{-3}]^{1/0.5}$

$= 6638.4$ gm/mol

7. PAA-VII

Table 2.7 Viscosity data for a PAA-VII in 1, 4-dioxane solution at RT

Sr. No.	Conc. (g/dl)	Time t(sec)	$\eta_r = t/to$	$\eta_{sp} = \eta_r - 1$	η_{sp}/C	$\ln(\eta_r)/C$
1	1,4-dioxane	t_o=110.18	-	-	-	-
2	0.01	117.35	1.0651	0.0651	6.5100	6.3067
3	0.008	115.87	1.0517	0.0517	6.4671	6.3053
4	0.006	114.35	1.0378	0.0378	6.3101	6.1838
5	0.004	113.76	1.0267	0.0267	6.2689	6.5874
6	0.002	111.55	1.0125	0.0125	6.2511	6.2123

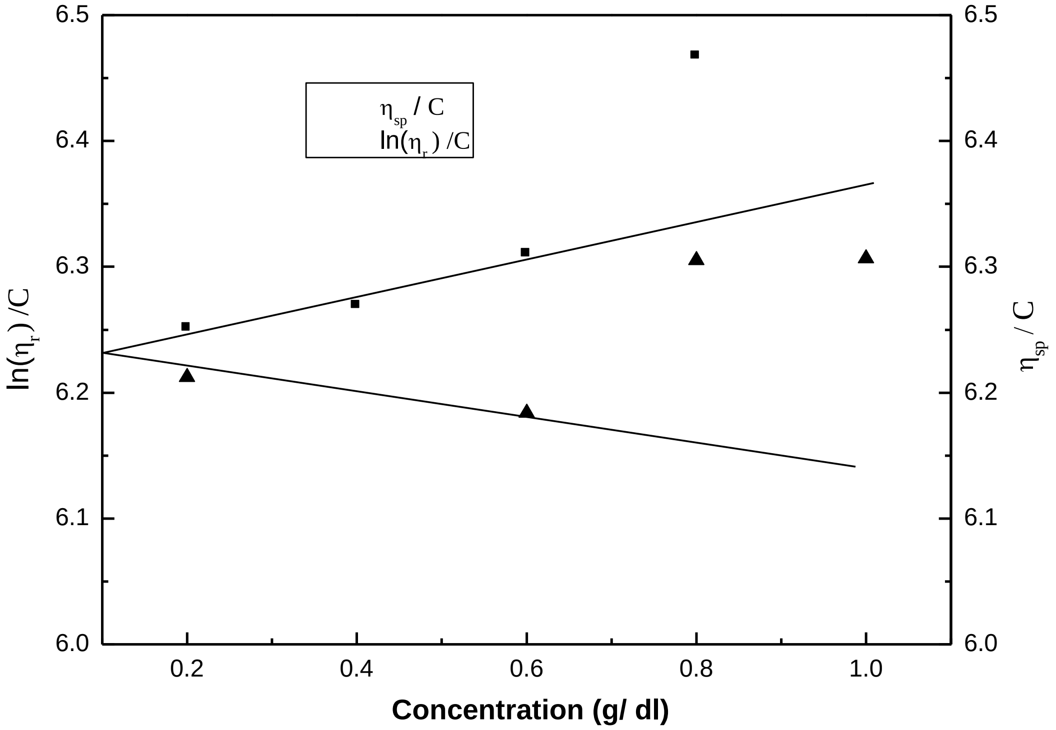


Figure 2.10 Plot for viscosity data for computing intrinsic viscosity [η] for PAA-VII

Mark-Houwink equation :

$[\eta] = K\, Mw^{a}$

$Mw = ([\eta] / K)^{1/a}$

Calculation :

$Mw = [6.2313/76x10^{-3}]^{1/0.5}$

$= 6722.5$ gm/mol

8. PAA-VIII

Table 2.8 Viscosity data for a PAA-VIII in 1, 4-dioxane solution at RT

Sr. No.	Conc. (g/dl)	Time t(sec)	η_r =t/to	η_{sp} =η_r- 1	η_{sp}/C	ln(η_r)/C
1	1,4-dioxane	t_o=110.18	-	-	-	-
2	0.01	116.78	1.0599	0.05989	5.9890	5.8165
3	0.008	115.38	1.0472	0.0472	5.9011	5.7660
4	0.006	113.97	1.0344	0.0344	5.7369	5.6403
5	0.004	112.69	1.0228	0.0228	5.7100	5.6457
6	0.002	111.46	1.0114	0.0114	5.6901	5.6579

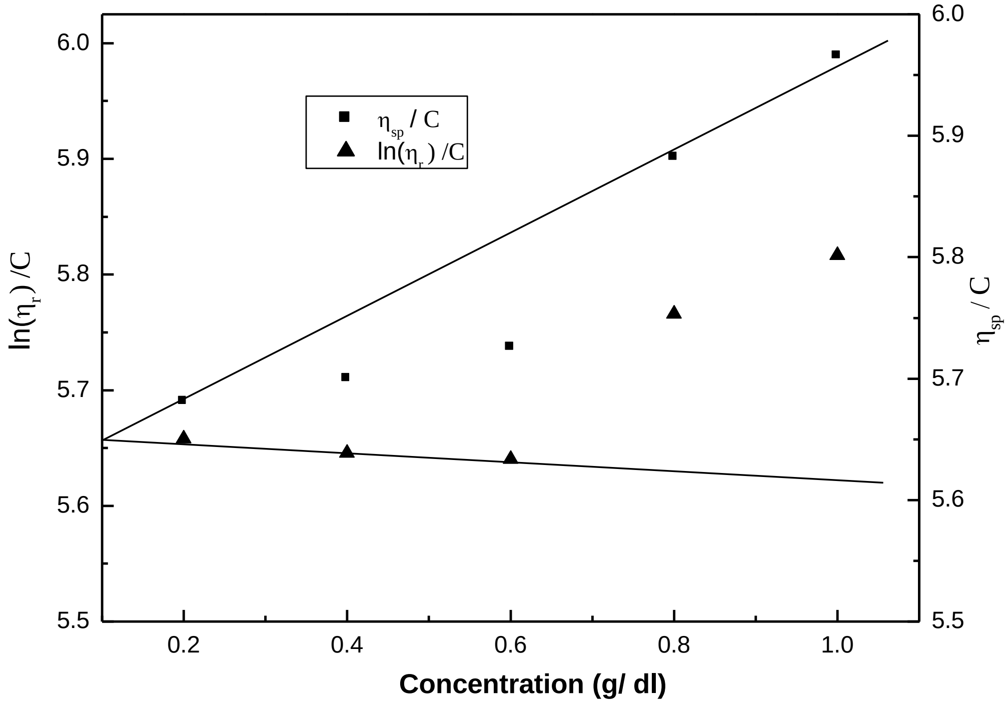


Figure 2.11 Plot for viscosity data for computing intrinsic viscosity [η] for PAA-VIII

Mark-Houwink equation : **Calculation :**

$[\eta] = K\,Mw^{a}$

$Mw = ([\eta] / K)^{1/a}$

$Mw = [5.6541/76x10^{-3}]^{1/0.5}$

$= 5534.8$ gm/mol

9. PAA-IX

Table 2.9 Viscosity data for a PAA-IX in 1, 4-dioxane solution at RT

Sr. No.	Conc. (g/dl)	Time t(sec)	η_r =t/to	η_{sp} =η_r- 1	η_{sp}/C	ln(η_r)/C
1	1,4-dioxane	t_o=110.18	-	-	-	-
2	0.01	116.70	1.0592	0.0592	5.9216	5.7514
3	0.008	115.15	1.0451	0.0451	5.6379	5.5144
4	0.006	113.75	1.0324	0.0324	5.4011	5.3154
5	0.004	112.57	1.0217	0.0217	5.4157	5.3579
6	0.002	111.37	1.0108	0.0108	5.4201	5.3909

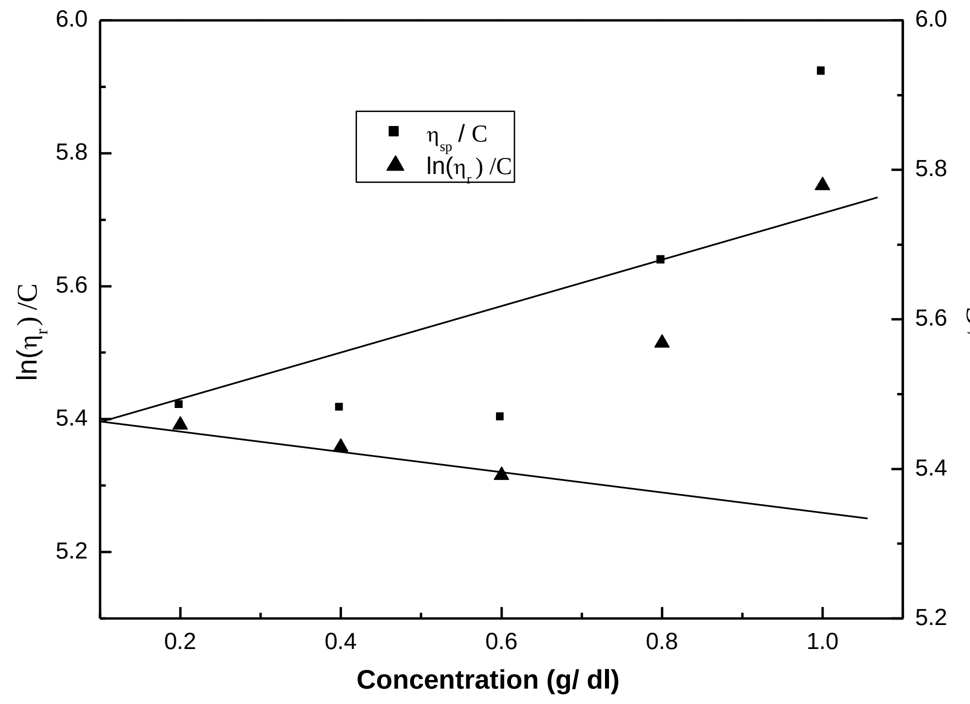


Figure 2.12 Plot for viscosity data for computing intrinsic viscosity [η] for PAA-IX

Mark-Houwink equation :

$[\eta] = K\ Mw^a$

$Mw = ([\eta] / K)^{1/a}$

Calculation :

$Mw = [5.4003/76x10^{-3}]^{1/0.5}$

$= 5049.0$ gm/mol

10. PAA-X

Table 2.10 Viscosity data for a PAA-X in 1, 4-dioxane solution at RT

Sr. No.	Conc. (g/dl)	Time t(sec)	η_r =t/to	η_{sp} =η_r- 1	η_{sp}/C	ln(η_r)/C
1	1,4-dioxane	t_o=110.18	-	-	-	-
2	0.01	116.239	1.0550	0.0550	5.5010	5.3541
3	0.008	114.995	1.0437	0.0437	5.4606	5.3465
4	0.006	113.772	1.0326	0.0326	5.4311	5.3466
5	0.004	112.566	1.0216	0.0216	5.4131	5.3425
6	0.002	111.357	1.0107	0.0107	5.3423	5.3216

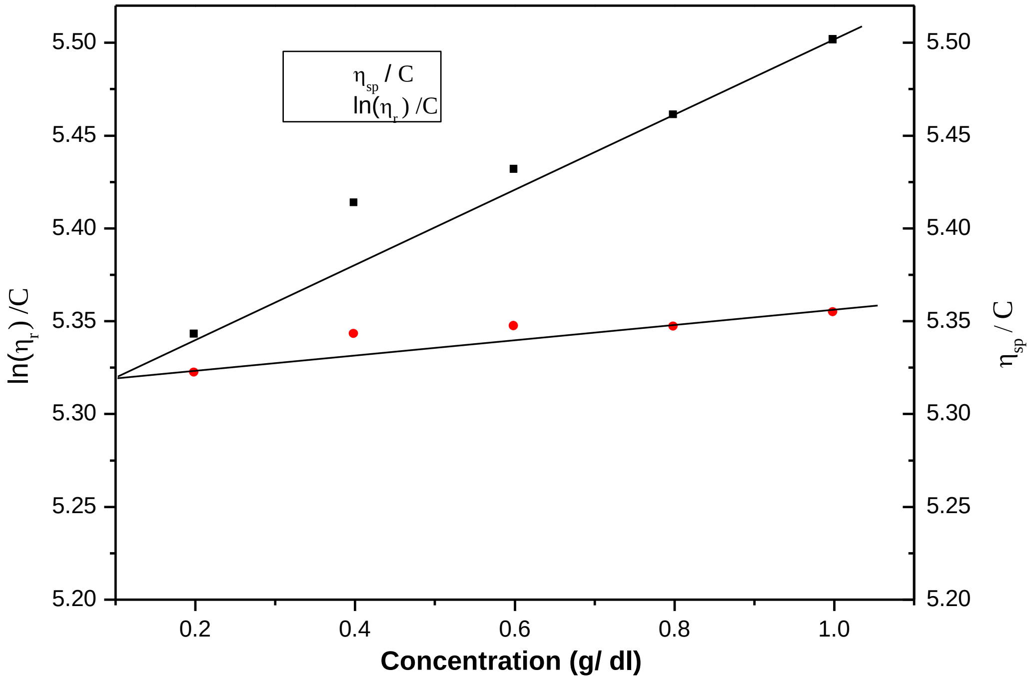


Figure 2.13 Plot for viscosity data for computing intrinsic viscosity [η] for PAA-X

Mark-Houwink equation :

$$[\eta] = K\,Mw^{a}$$

$$Mw = ([\eta]/K)^{1/a}$$

Calculation :

$$Mw = [5.3198/76\text{x}10^{-3}]^{1/0.5}$$

$$= 4899.6\ \text{gm/mol}$$

(B) Viscosity Diagram for PAA samples from variation in concentration of Allyl alcohol (inhibitor):-

1. PAA-XI : Table 2.11 Viscosity data for a PAA-XI in 1, 4-dioxane solution at RT

Sr. No.	Conc. (g/dl)	Time t(sec)	η_r =t/to	η_{sp} =η_r- 1	η_{sp}/C	ln(η_r)/C
1	1,4-dioxane	t_o=110.18	-	-	-	-
2	0.01	122.10	1.1082	0.1082	10.8225	10.2759
3	0.008	119.58	1.0853	0.0853	10.6696	10.2386
4	0.006	117.11	1.0629	0.0629	10.4811	10.1647
5	0.004	114.78	1.0418	0.0418	10.4429	10.2306
6	0.002	112.43	1.0203	0.0203	10.1944	10.0918

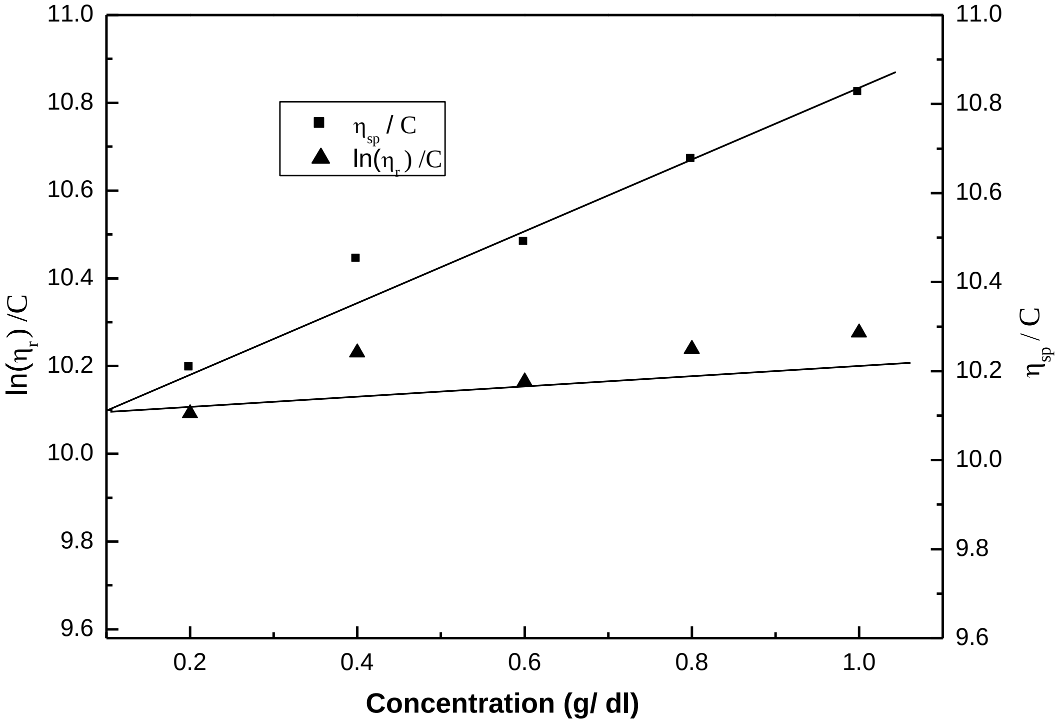


Figure 2.14 Plot for viscosity data for computing intrinsic viscosity [η] for PAA-XI

Mark-Houwink equation :

$[\eta] = K\ Mw^{a}$

$Mw = ([\eta] / K)^{1/a}$

Calculation :

$Mw = [10.0982/76x10^{-3}]^{1/0.5}$

$= 17654.7$ gm/mol

2. PAA-XII

Table 2.12 Viscosity data for a PAA-XII in 1, 4-dioxane solution at RT

Sr. No.	Conc. (g/dl)	Time t(sec)	$\eta_r = t/to$	$\eta_{sp} = \eta_r - 1$	η_{sp}/C	$\ln(\eta_r)/C$
1	1,4-dioxane	t_o=110.18	-	-	-	-
2	0.01	121.04	1.0985	0.0985	9.8531	9.3974
3	0.008	118.79	1.0782	0.0782	9.7793	9.4156
4	0.006	116.62	1.0584	0.0584	9.7411	9.4670
5	0.004	114.44	1.0386	0.0386	9.6647	9.4826
6	0.002	112.29	1.0192	0.0192	9.5882	9.4974

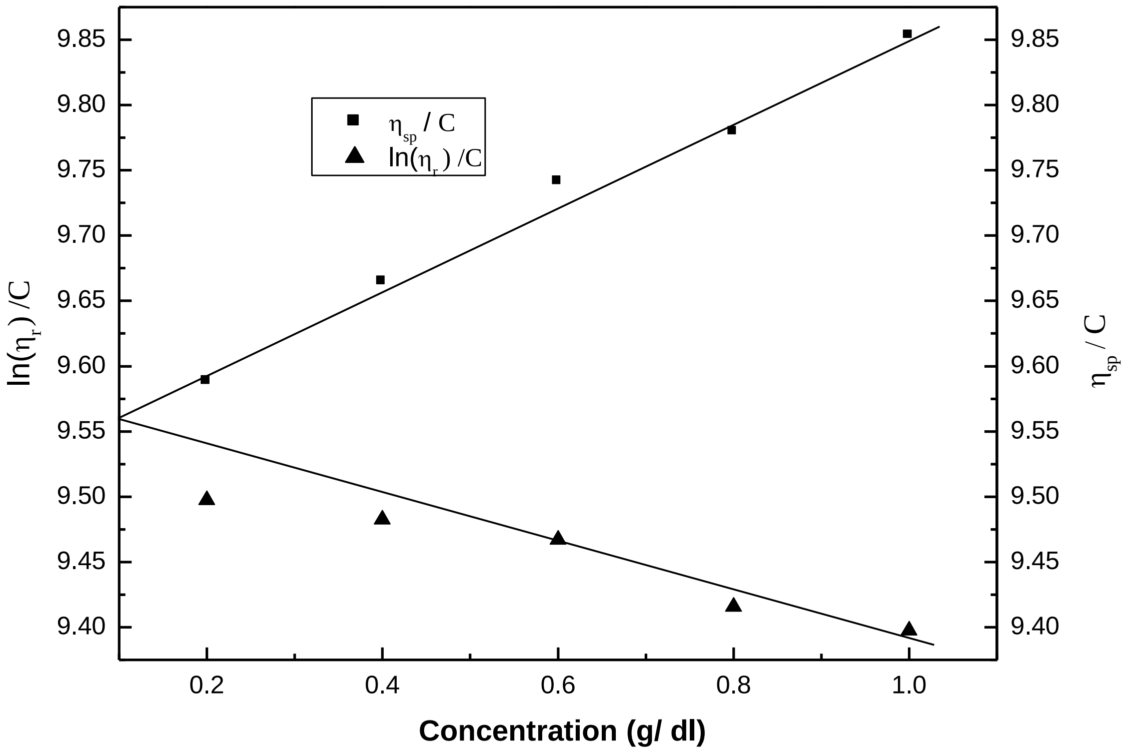


Figure 2.15 Plot for viscosity data for computing intrinsic viscosity [η] for PAA-XII

Mark-Houwink equation :

$[\eta] = K\, Mw^a$

$Mw = ([\eta] / K)^{1/a}$

Calculation :

$Mw = [9.5597/76x10^{-3}]^{1/0.5}$

$= 15821.9$ gm/mol

3. PAA-XIII

Table 2.13 Viscosity data for a PAA-XIII in 1, 4-dioxane solution at RT

Sr. No.	Conc. (g/dl)	Time t(sec)	η_r =t/to	η_{sp} =η_r- 1	η_{sp}/C	ln(η_r)/C
1	1,4-dioxane	t_o=110.18	-	-	-	-
2	0.01	120.03	1.0894	0.0894	8.9377	8.5606
3	0.008	117.98	1.0708	0.0708	8.8476	8.5485
4	0.006	115.98	1.0527	0.0527	8.7788	8.5554
5	0.004	114.01	1.0347	0.0347	8.6887	8.5411
6	0.002	112.07	1.0172	0.0172	8.6199	8.5269

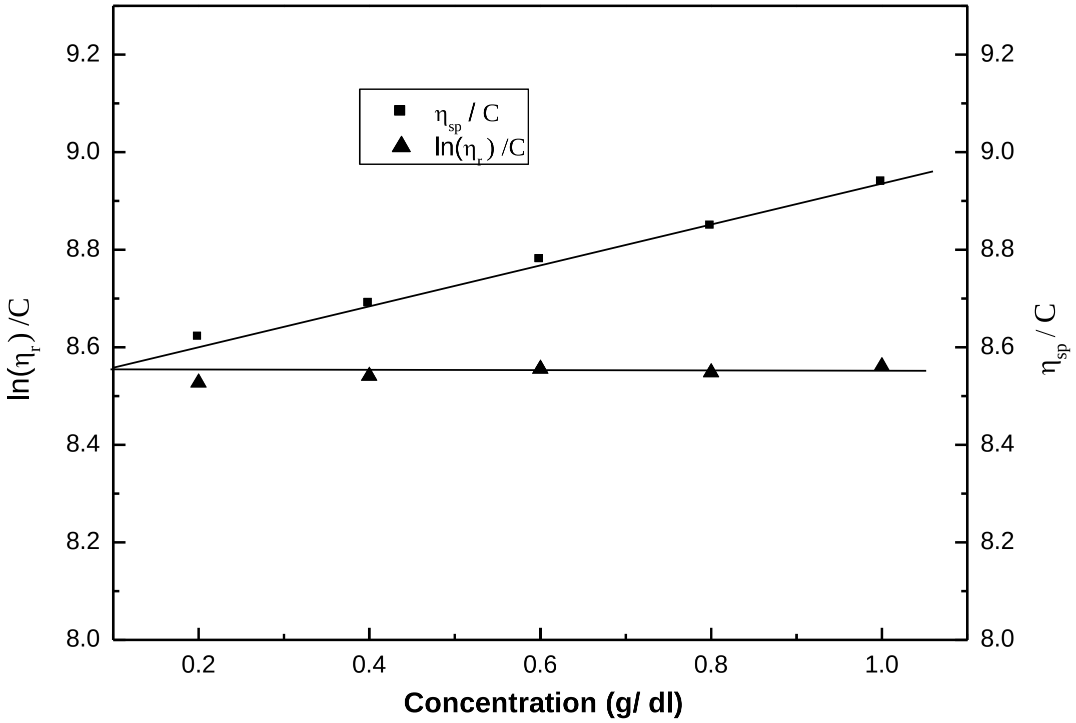


Figure 2.16 Plot for viscosity data for computing intrinsic viscosity [η] for PAA-XIII

Mark-Houwink equation :

$[\eta] = K\ Mw^{a}$

$Mw = ([\eta] / K)^{1/a}$

Calculation :

$Mw = [8.5613/76x10^{-3}]^{1/0.5}$

$= 14964.3$ gm/mol

Viscosity Diagram for PAA samples from variation in concentration of Allyl chloride (inhibitor):-

1. PAA-XIV:Table 2.14 Viscosity data for a PAA-XIV in 1, 4-dioxane solution at RT

Sr. No.	Conc. (g/dl)	Time t(sec)	$\eta_r = t/to$	$\eta_{sp} = \eta_r - 1$	η_{sp}/C	$\ln(\eta_r)/C$
1	1,4-dioxane	t_o=110.18	-	-	-	-
2	0.01	122.06	1.1078	0.1078	10.7842	10.2414
3	0.008	119.52	1.0847	0.0847	10.5931	10.1681
4	0.006	116.96	1.0615	0.0615	10.2518	9.9472
5	0.004	114.66	1.0407	0.0407	10.1753	9.9737
6	0.002	112.38	1.0199	0.0199	9.9678	9.8697

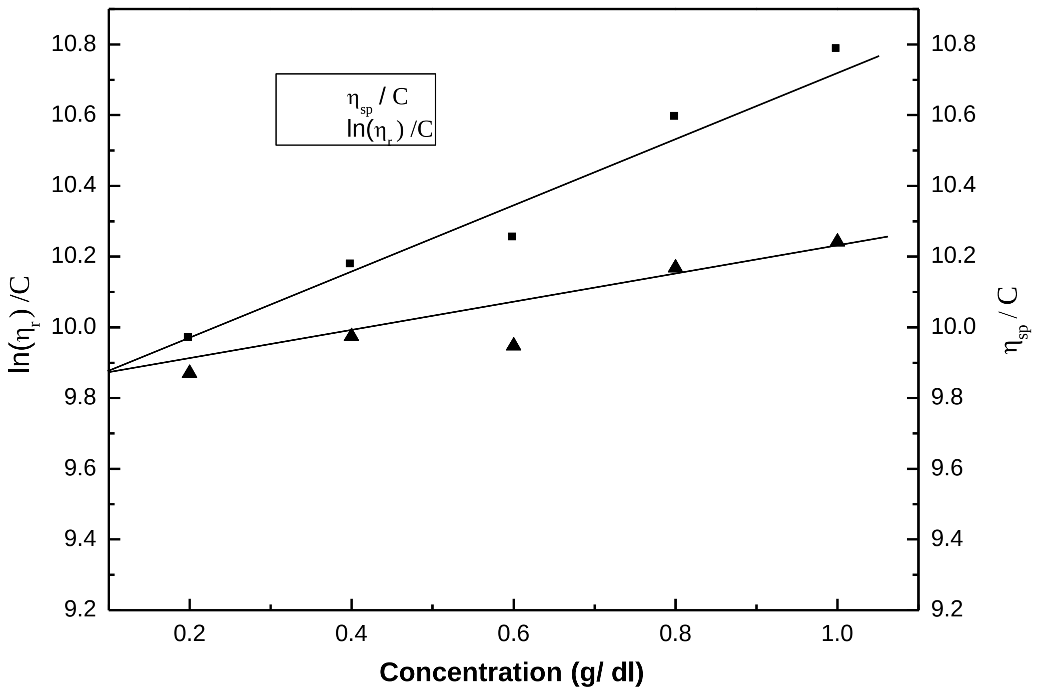


Figure 2.17 Plot for viscosity data for computing intrinsic viscosity [η] for PAA-XIV

Mark-Houwink equation:

$[\eta] = K\,Mw^{a}$

$Mw = ([\eta] / K)^{1/a}$

Calculation :

$Mw = [9.8805/76x10^{-3}]^{1/0.5}$

$= 16901.7$ gm/mol

2. PAA-XV

Table 2.15 Viscosity data for a PAA-XV in 1, 4-dioxane solution at RT

Sr. No.	Conc. (g/dl)	Time t(sec)	$\eta_r = t/to$	$\eta_{sp} = \eta_r - 1$	η_{sp}/C	$\ln(\eta_r)/C$
1	1,4-dioxane	t_o=110.18	-	-	-	-
2	0.01	122.03	1.1076	0.1076	10.7651	10.2195
3	0.008	119.37	1.0834	0.0834	10.4238	10.0130
4	0.006	116.84	1.0605	0.0605	10.0824	9.7892
5	0.004	114.46	1.0388	0.0388	9.7029	9.5193
6	0.002	112.26	1.0189	0.0189	9.4544	9.3661

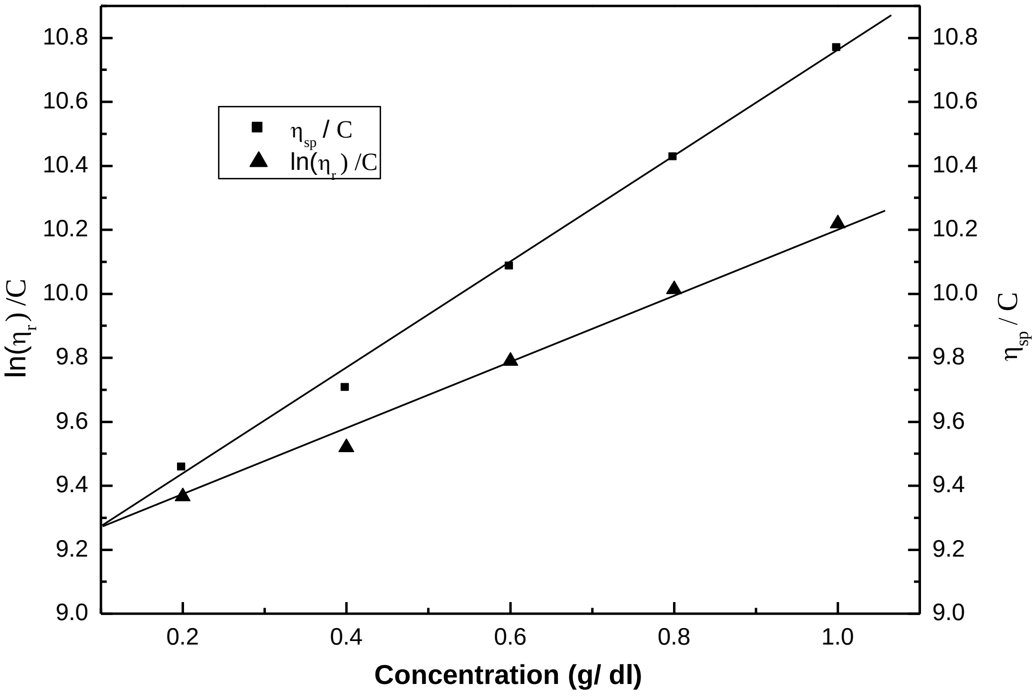


Figure 2.18 Plot for viscosity data for computing intrinsic viscosity [η] for PAA-XV

Mark-Houwink equation :

$[\eta] = K\, Mw^{a}$

$Mw = ([\eta] / K)^{1/a}$

Calculation :

$Mw = [9.2709/76x10^{-3}]^{1/0.5}$

$= 14880.5$ gm/mol

3. PAA-XVI

Table 2.16 Viscosity data for a PAA-XVI in 1, 4-dioxane solution at RT

Sr. No.	Conc. (g/dl)	Time t(sec)	$\eta_r = t/t_o$	$\eta_{sp} = \eta_r - 1$	η_{sp}/C	$\ln(\eta_r)/C$
1	1,4-dioxane	t_o=110.18	-	-	-	-
2	0.01	120.12	1.0902	0.0902	9.0202	8.6363
3	0.008	117.96	1.0706	0.0706	8.8290	8.5311
4	0.006	116.00	1.0528	0.0528	8.8099	8.5849
5	0.004	113.93	1.0340	0.0340	8.5068	8.3653
6	0.002	112.01	1.0166	0.0166	8.3184	8.2499

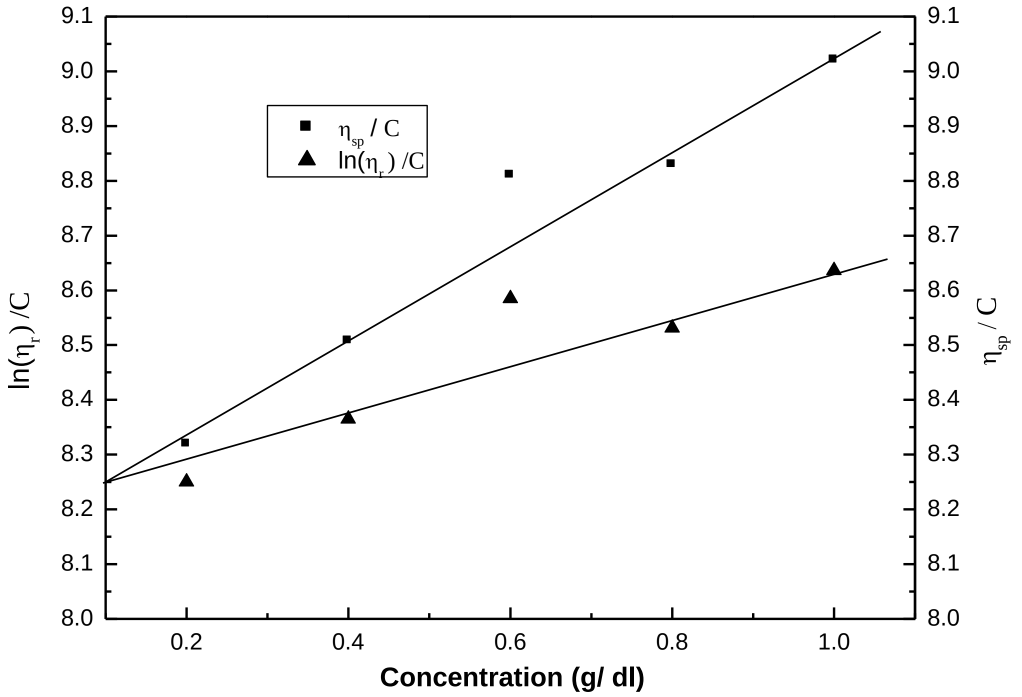


Figure 2.19 Plot for viscosity data for computing intrinsic viscosity [η] for PAA-XVI

Mark-Houwink equation :

$[\eta] = K\,Mw^{a}$

$Mw = ([\eta]/K)^{1/a}$

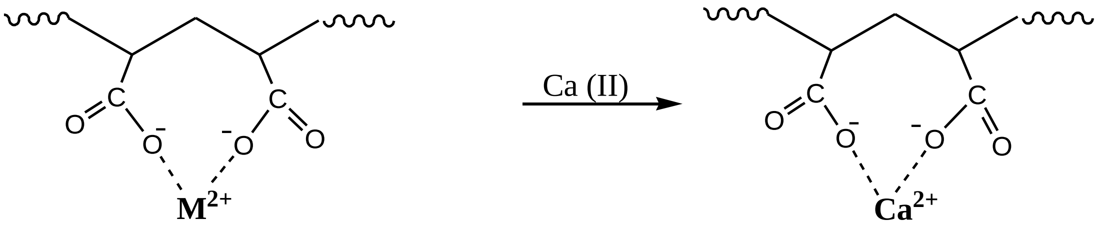
Calculation :

$Mw = [8.2501/76\text{x}10^{-3}]^{1/0.5}$

$= 11783.95$ gm/mol

2.3.3 Metallic Sequestration Capability Study

These synthesized PAA's were also characterized for its metallic sequestration capability which is useful for toxic metal removal during waste water treatment. However, in our working conditions, the longer PAA chains are folded to a certain degree and the carboxylic functions are not all exposed[50]. Most of them are embedded in the core, and consequently, the sequestration of the metallic ions, by the carboxylic groups is not quantitative[51,52]. In the case of shorter PAA chains, the unfolding is more accessible and prone to the complexation with metallic ions. One of the mechanisms by which polymers prevent scaling is the sequestration of metallic ions which involves complex formation with metallic ions. Sequestration value is inversely proportional to molecular weight. However Fig. 2.20 represents that how PAA sequester metal ions from its solution.



(PAA complex M^{2+} : Ca^{2+}, Fe^{2+}, Sr^{2+} etc.)

Figure 2.20 Schematic representation of metallic sequestration through PAA

Table 2.17, 2.18 & 2.19 consists the sequestration value and molecular weights of synthesized PAA samples whereas Fig. 2.21 and 2.22 shown that how sequestration capability was increases with decrease in molecular weight. So as low as the molecular weight of polymer it sequesters more metallic ions from its aqueous solution[53-55].

Table 2.17 Composition of reactants with sequestration value & Molecular weight of PAAs

Sample	Acrylic acid (ml)	Water (ml)	Initiators %		Sequestration value	Molecular Weight (M_n) (gm/mol)
			L-ascorbic acid (*%)	H_2O_2 (*%)		
I	20	100	5	5	471	12218
II	20	100	10	10	519	9242
III	20	100	15	15	548	8733
IV	20	100	20	20	573	7927
V	20	100	25	25	598	7330
VI	20	100	30	30	623	6638
VII	20	100	35	35	654	6722
VIII	20	100	40	40	693	5534
IX	20	100	45	45	731	5049
X	20	100	50	50	759	4899

*weight % of monomer

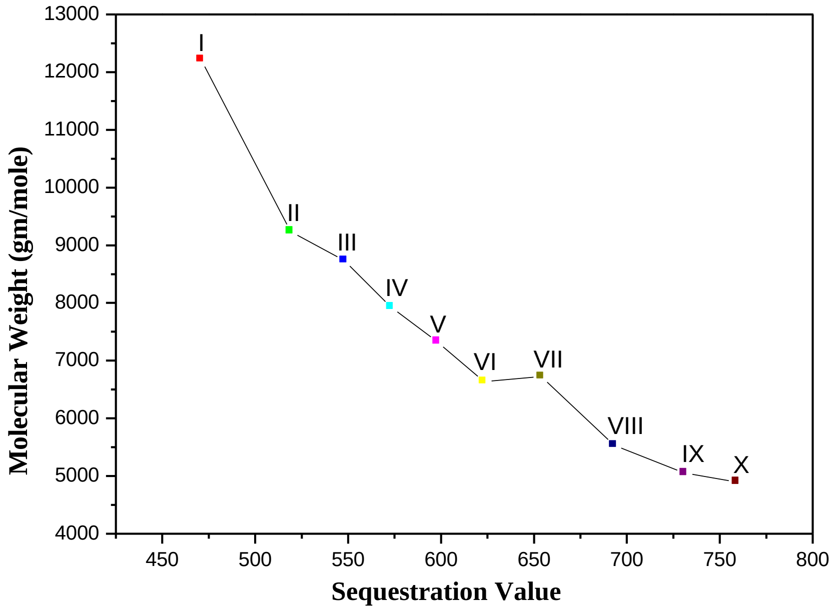


Figure 2.21 Graphical representation of relation between molecular weight & metallic sequestration

Table 2.18 For Allyl Alcohol: Composition of reactants with sequestration value & Molecular weight of PAAs

Sr. No.	Acrylic acid (ml)	Allyl alcohol (ml)	H_2O (ml)	L-Ascorbic acid (%)	H_2O_2 (%)	Sequestration Value	Molecular Weight (M_n)
1.	19	1	50	5	10	283	17654
2.	15	5	50	5	10	322	15821
3.	10	10	50	5	10	371	14964

Table 2.19 For Allyl Chloride: Composition of reactants with sequestration value & Molecular weight of PAAs

Sr. No.	Acrylic acid (ml)	Allyl Chloride (ml)	H_2O (ml)	L-Ascorbic acid (%)	H_2O_2 (%)	Sequestration Value	Molecular Weight (M_n)
1.	19	1	50	5	10	301	16901
2.	15	5	50	5	10	374	14880
3.	10	10	50	5	10	429	11783

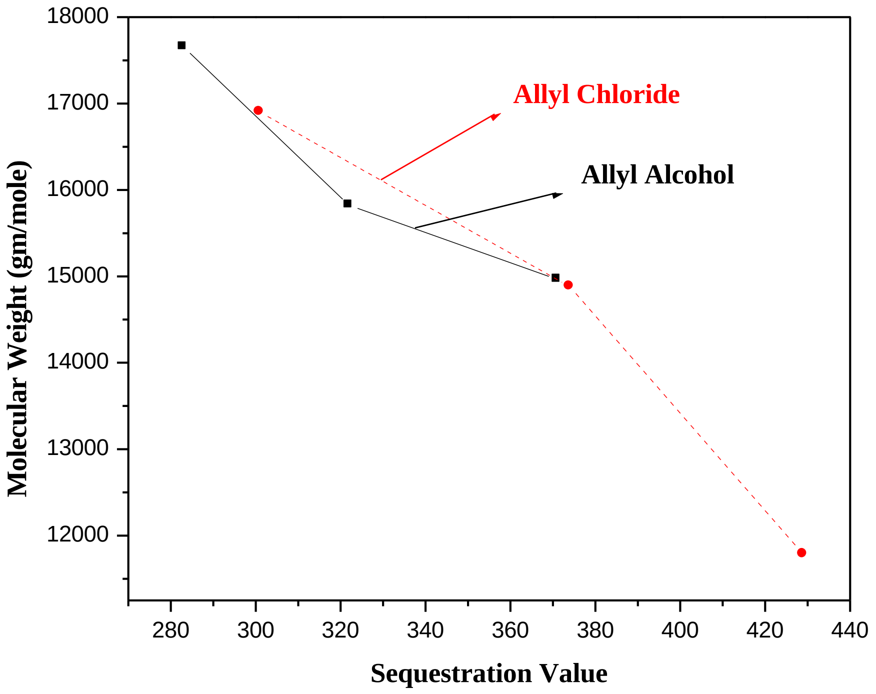


Figure 2.22 Graphical representation of relation between molecular weight & metallic sequestration

2.4 Conclusions

So from this chapter it can be concluded that as we increase the concentration of initiator it provides more free radicals or reactive sites so form more number of initiating radicals which results in more number of termination by coupling. Thus it forms more number of small polymer chains/molecules. And same in case of inhibitors also, as we increase the concentration of inhibitor it terminates the more number of growing chain so form more number of small polymer molecules. Since we already know that the molecular weight of polymers are calculated as the average molecular weight of its polymer chain molecules so as the number of shorter polymer chain increases automatically the molecular weight of polymer decreases and thus it produces a low molecular weight polymers. These low molecular weight poly(acrylic acid) showed significant abilities to recover different metal ions from their aqueous solutions which can be applied in many application directions such as toxic metal ion removal in waste water treatment plants.

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