

**INTERNATIONAL JOURNAL OF ADVANCES IN
PHARMACY, BIOLOGY AND CHEMISTRY****Research Article****Salicylic Acid – Formaldehyde Oligomer
- Viscometric Study****K.M.Darji¹, D.R.Patel², G.D.Acharya³.**¹Hathoj Primary School, Hathoj, Gujarat, India-383215.²Municipal Arts & Urban Science College, Mehsana, Gujarat, India- 384002.³Head, Dept. of Chemistry, R.R.Mehta College of Science & C.L.Parikh College of
Commerce, Palanpur, Gujarat, India-385001.**Abstract**

Viscosity measurement of solution of Salicylic acid- formaldehyde oligomer and its fractions were carried out in DMF at $30^{\circ} \pm 0.3^{\circ}\text{C}$. Viscosity measurement was carried out in Ubbelohde viscometer. Salicylic acid- formaldehyde oligomer (mol. Wt.= 6000 gm/mole) was prepared by reported method. The viscosity data of the solution of SF oligomer signified that the decrease in concentration of solution increases reduced viscosity (η_{red}). This suggests the SF oligomer act as polyelectrolyte of anionic type. Thus the viscosity of the solution in DMF suppresses by adding water and KBr in DMF. Thus the viscosity measurement of solution of SF oligomer in DMF-Water-KBr(80:20:1%) gives the intrinsic viscosity by applying empirical equation.

Keywords: Salicylic acid- formaldehyde oligomer, Polyelectrolyte, Ubbelohde viscometer, reduced viscosity, empirical relation and intrinsic viscosity.

INTRODUCTION

Polymer with positive or negative charges on its repeating units is known as Polyelectrolyte. It dissociates in solution, forming a charged polyion surrounded by an atmosphere of small, mobile counterions^{1,2}. Both the repulsive and the attractive electrostatic interactions between these charged species represent dominant factors influencing the properties of polyelectrolytes in solution. Moreover, if ionic polymer contains hydrophobic structural components, then these polymers, called amphiphilic polyelectrolytes, exhibit solution properties resulting from the competition between the hydrophobic and electrostatic interactions^{3,4}. Polyelectrolyte can be effects arising from intra-chain electrostatic forces between charges presented on the chain backbone. For example, the famous phenomenon of upward bending of reduced viscosity versus the concentration plot of electrolyte solution in the dilute concentration region is ascribed to the intra-chain electrostatic repulsion of charges on the same backbone. This also leads to

chain extension and an increase of reduced viscosity upon dilution^{5,6}. Besides the theoretical interest, both the electrostatic and hydrophobic interactions play an important role in biological systems as well as in technological and environmental applications, such as: paper processing, film coating, flocculants, biomedical devices and drug formulations, membranes, and so on⁷. These interactions are strongly sensitive to some parameters, like: the chain length, the charge density, the polyelectrolyte concentration, the counter ion type, the ionic strength, the solvent polarity, the length and content of hydrophobic groups, etc^{8,9}.

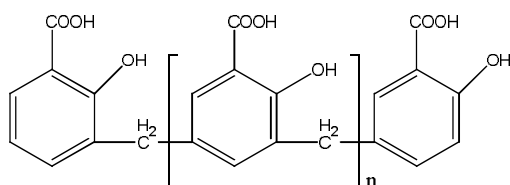
One of the condensation polymer say, salicylic acid-formaldehyde polymer was reported for the application like ion-exchange resin^{10,11}, tanning agents^{12,13}, a binder for printing ink¹⁴ and corrosion inhibitor¹⁵. As anionic polymer, its viscometric behaviour has not been studied academically except one instance¹⁶. Thus it was thought to explore field of

SF polyelectrolytes in organic solvents. So the present communication comprises the study of viscometric polyelectrolyte behaviour of SF oligomer and its fractions in DMF solvent.

EXPERIMENTAL

Materials:

Salicylic acid-formaldehyde oligomer was prepared by reported method. It was fractionated by fractional precipitation method and its general structure shown in below scheme 1. DMF was purified by reported method¹⁷. Distilled water and recrystallized KBr were used. Ubbelohde suspended type viscometer was used for all the experiments. The viscometer bath was used with maintaining temperature $30^{\circ} \pm 0.3^{\circ}\text{C}$.



Scheme 1: General structure of SF oligomer

Viscosity Measurement:

The relative, specific and reduced viscosity of the SF oligomer solutions from the flow times of solutions was measured by using the Ubbelohde capillary viscometer. The viscosity measurements were carried out at a constant temperature of $30^{\circ} \pm 0.3^{\circ}\text{C}$. The temperature of solution was controlled by a thermostat in a circulating bath and monitored by the thermometer. A stopwatch with a resolution of 0.1s was used to measure the flow times. By plotting the reduced viscosity (dL/g) of polymer solutions against concentration (g/dL), extrapolating to infinite dilution and taking the intercept, the intrinsic viscosity $[\eta]$ is determined.

RESULTS AND DISCUSSION

The reduced viscosity of the SF oligomer solution in the DMF solvent is shown in Figure 1 as a function of polymer concentration. It is seen from Figure 1 that the reduced viscosity increases with the decreasing polymer concentration. This typical polyelectrolyte behaviour like this for the reason that the carboxylic groups on the polymer chain can ionize in the polar solvent and also the effective electrostatic repulsion makes this polymer chain highly extended^{18,19}. In this case measurement could not be performed at sufficiently low concentrations owing to the comparatively low viscosity of these solutions. The polyelectrolyte either cationic or anionic polymers have special viscosity behaviour in association with neutral polymer. Neutral polymers

have the properties that reduce viscosity increases with the increase of polymer concentration.

The effort was finished to determine the viscosity in mixed form of DMF and water (80:20) solvent system. The results are also parity to neat solvent. This may be caused by addition of water the ionization of polyelectrolyte decreases due to the dielectric constant. The dielectric constant has a significant effect on the strength and range of electrostatic interactions²⁰.

Figure 2 shows the reduced viscosity as a function of polymer concentration in the presence of 1,4-dioxane-water-KBr (80:20:1%). The mechanism of the KBr effect on reducing the polyelectrolyte effect mainly is related to the reduction of double layer thickness on the polyelectrolyte molecule. Due to high degree of ionization, KBr reduces the partial ionization of polyelectrolyte and eliminates the polyelectrolyte effect at lower concentration. When small molecule electrolyte is added to the polyelectrolyte solution depending on the concentration, the viscosity behaviour changes²¹. It is seen from Figure 2 that there is not electrolyte effect and viscosity does not increase with decreasing polymer concentration, which is in contrast with salt-free solution.

It was noted that 1.0% solution of this polymer in dioxane was fairly good conductors of electricity. This indicated that the polymers behave as weak electrolytes in these solvents.

Viscosity of a given solution of a rigid polymer depends upon the interactions between the polymer chain and upon the hydrodynamic volume of the polymer. In the present case the solution contains a polycarboxylate ion. Because of lower shielding of the COO^- ions present in the polymer chains, the polymer chains will keep away from each other to minimize the repulsive interaction. With increase in dilution, the number of solvent molecules per molecules of polymer chain would increase. Hence number of solvent molecules surrounding each ion on polymer chain would increase. The repulsive interaction of polymer chain would decrease. Due to association of COO^- with larger number of solvent molecules the hydrodynamic volume would also increase. With increase in dilution the strength of repulsive interaction decreases and the hydrodynamic volume increases. As a result the viscosity functions would increase with decrease in concentration of polymer solutions.

In case a circumstance is produced such that, (a) The negatively charged ion is well surrounded by an equal number of both +ve and -ve ions, the polyelectrolytic behaviour will not be observed. This situation is created by adding a strong electrolyte to the solvent

in which the viscometry is carried out. (b) The negatively charged ions of the polyionic species are very well solvated even in concentrated solution to the extent that, on further dilution there is no additional solvation or protection. This situation is created by increasing the solvent power of the solvent e.g. by using a mixture like dioxane – water mixture as solvent in place of a pure solvent.

Application of empirical relation to the data:

The empirical relation is,

$$\eta_{sp}/c = Z = [\eta] + \frac{K[\eta]}{C^{1/2}}$$

The application of the equation to the data has been examined and the results are represented in the **Table 3**. The plots are shown in **Figure 3**, this was indicated that the plots were linear. The above mentioned empirical equation is able to represent the empirical

data for all the polymers. It may be stated that as the equation is quite empirical.

CONCLUSION

The intrinsic viscosity has been determined by extrapolating the reduced viscosity to zero concentration. The effects of solvent (1,4-dioxane), solvent-water, and solvent-water-KBr on viscosity have been investigated. It was shown that the reduced viscosity of 1,4-dioxane using solution of SF oligomer as a result of polymer chain expansion increases with decreasing polymer concentration. In fact the polymer behaves like a polyelectrolyte in salt-free solution. The effect of water on reduced viscosity was studied and it was found that reduced viscosity decreases with the mixing of water content in to the solvent. Adding of low molecular weight electrolyte (KBr) to the polymer solution eliminates the polyelectrolyte effect and polymer behaves like a neutral macromolecule. The viscosity decreases with decrease the polymer concentration, which is usually observed in neutral polymers.

Table 1
Reduce viscosity of solution of SF oligomer using DMF.

Polymer Samples	Reduced Viscosity (η_{red} dL/g) at concentration, (C g/dL)				
	3.000	2.142	1.666	1.363	1.152
Conglomerated SF	0.04698	0.04645	0.04717	0.04842	0.04936
SF 1	0.05937	0.05829	0.05892	0.05994	0.06453
SF 2	0.05352	0.05221	0.05429	0.05761	0.05998
SF 3	0.04062	0.04114	0.04173	0.04497	0.04613

Table 2
Reduce viscosity of solution of SF oligomer using DMF-water-KBr (80:20:1 %).

Polymer Samples	Reduced Viscosity (η_{red} dL/g) at concentration, (C g/dL)					Intrinsic Viscosity [η] $\times 10^2$	Slop of linear plot K $\times 10^3$
	3.000	2.142	1.666	1.363	1.152		
Conglomerated SF	0.04337	0.04035	0.03987	0.038083	0.03779	3.31	2.70
SF 1	0.05051	0.04838	0.04877	0.04772	0.04643	4.36	1.97
SF 2	0.04358	0.042484	0.04179	0.04141	0.04104	3.92	1.45
SF 3	0.03085	0.03012	0.02970	0.02953	0.02936	2.83	0.84

Table 3
Reduce viscosity of solution of SF oligomer using DMF.

Polymer Samples	Reduced Viscosity (η_{red} dL/g) vs $1/C^{1/2}$					Intrinsic Viscosity [η] $\times 10^2$
	0.577	0.683	0.774	0.856	0.931	
Conglomerated SF	0.05308	0.05357	0.05436	0.05509	0.05755	4.94
SF 1	0.06490	0.06520	0.06521	0.06569	0.06604	6.36
SF 2	0.04639	0.04625	0.04687	0.04707	0.04756	4.43
SF 3	0.03618	0.03623	0.03628	0.03664	0.03846	3.53

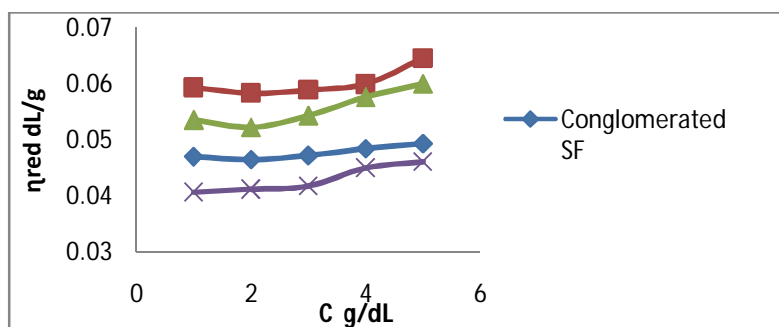


Figure 1
Reduced Viscosity vs Concentration of SF oligomer using DMF.

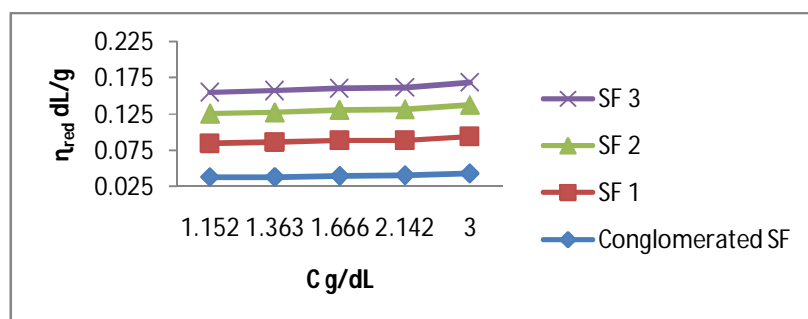


Figure 2
Reduced Viscosity vs Concentration of SF oligomer using DMF-water-KBr(80:20:1%).

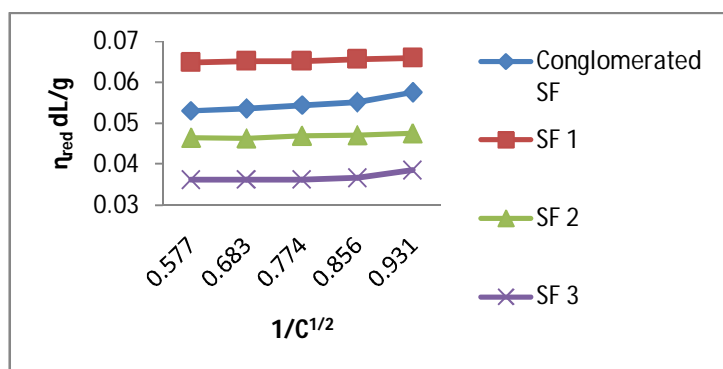


Figure 3
Reduced Viscosity vs $1/C^{1/2}$ of SF oligomer using DMF.

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