Viscometric study of carboxymethyl phenol-formaldehyde resins

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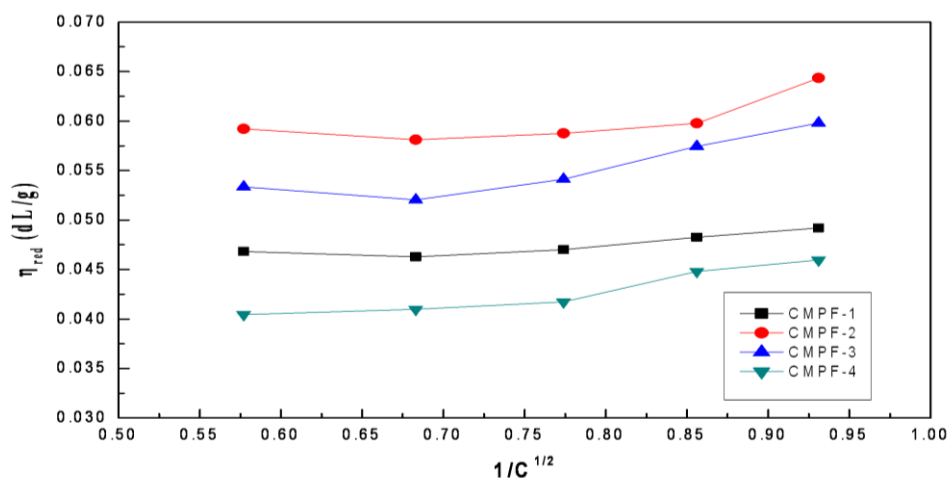Corresponding Auther's E-mail Address:bhlu86@yahoo.com

- **Novelty and Highlights:**

  1 –Viscosity measurements of solutions of Carboxymethyl Phenol- formaldehyde (CMPF) resins.

  2 –The reduced viscosity of DMF using solution of CMPF resins as a result of polymer chain expansion increases with decreasing polymer concentration.

  3 –The viscosity decreases with decrease the polymer concentration, which is usually observed in neutral polymers.

- **Graphical Abstract:**

  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.

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Abstract: Viscosity measurements of solutions of carboxymethyl phenol-formaldehyde (CMPF) resins were carried out in DMF at $30^o \pm 0.3^oC$ by using Ubbelohde viscometer. CMPF resins were prepared by reported method. The viscosity data of the solution of CMPF resins signified that the decrease in concentration of solution increases reduced viscosity ($ŋ_{red}$). This suggests the CMPF resins act as polyelectrolyte of anionic type. Therefore the viscosity of the solution in DMF is suppressed by adding water and KBr in DMF. Thus the viscosity measurements of solution of CMPF resins in DMF-Water-KBr(80:20:1%) gives the intrinsic viscosity. Also applying empirical equation:

$$ŋ_{sp/C} = Z = [ŋ] + \frac{K^{[ŋ]}}{C^{1/2}}$$

is able to represent the viscometric data for the resins. It may be stated that as the equation is quite empirical.

Keywords: *Polyelectrolyte, Phenol- formaldehyde resin, Ubbelohde viscometer, reduced viscosity, empirical relation and intrinsic viscosity.*

Introduction:

Polyelectrolyte carried positive or negative charges on these repeating units. By dissociation there in solution, form a charged polyion surrounded by an atmosphere of small, mobile counter ions [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, 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 well-known behaviour of upward bending of reduced viscosity versus the concentration plot of electrolyte solution in the dilute concentration region is designated to the intra-chain electrostatic repulsion of charges on the same polymer skeleton. This also affects 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 on [7]. 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].
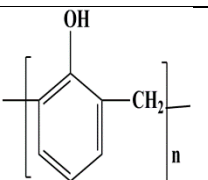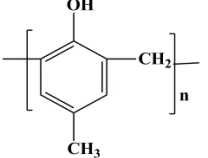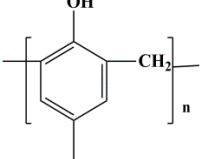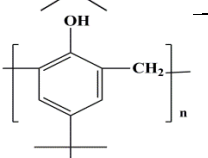
One of the resins called Carboxymethyl Phenol-formaldehyde resin having versatile applications. Its carboxy methyl derivatives designated as carboxymethyl Phenol formaldehyde resin (CMPF) has been reported for application like ion-exchange resin [10, 11], tanning agents [12, 13], a binder for printing ink [14] and corrosion inhibitor [15].As anionic polymer, its viscometric behaviour has not been studied academically. Thus it was thought to explore field of CMPF polyelectrolytes in organic solvents. So the present work comprises the study of viscometric polyelectrolyte behaviour of various CMPF resins.

Experimental

Materials: Phenol- formaldehyde PF resins listed in Table-1 were prepared by reported method [16]. All of the chemical used were of pure grade. The viscometer bath was used with maintaining temperature $30^o \pm 0.3^oC$.

Synthesis of Carboxymethyl PF resins: All the four PF resins were treated with monochloro acetic acid to afford carboxymethyl PF resin. The method was adopted as method reported for caboxymethyl cellulose. The general procedure is as follow.

Table 1:Phenol-Formaldehyde resins

Polymer sample	PF resin	structure
1	Phenol-Formaldehyde resin	
2	4 methyl- Phenol-Formaldehyde resin	
3	4 iso propyl Phenol-Formaldehyde resin	
4	4 tert butyl Phenol-Formaldehyde resin	

To a solution of PF **(Table-1)** resins (Listed in Table-2) in acetone was added by 0.1 M Sodium methoxide dissolved in methanol. The suspended pasty mass was obtained. To this resultant mass the solution of monochloro acetic acid in water added stoichiometrcally. The solid precipitates of carboxymethyl PF resin was obtained, filtered, washed by petroleum ether and air dried. The products were designated as CMPF 1 to 4. Their details are furnished in Table-2.The detail scheme-1 is as follow.
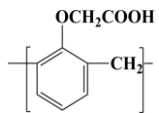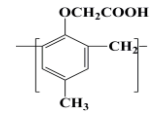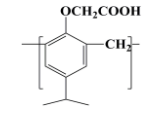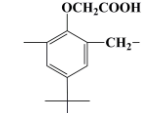
The non-aqueous conductmetric titration of all the resins measured in pyridine ageist tetra-n-butyl ammonium hydroxide in pyridine as titrate**.** The number average molecular weight of all the four resigns was estimated by Vapour Pressure Osmometer (VPO) Knauer K7000 in DMF at $70^o \pm 0.1^oC$ **(Table-3)**.The infrared spectra (FT-IR) were obtained from KBr pellets in the range 4000–400 cm^{-1} with a Perkin Elmer spectrum GX spectrophotometer (FT–IR) instrument. The TGA of all resins were carried out with a model Perkin Elmer thermogravimetry analyser at a heating rate of 10 $^{\circ}Cmin^{-1}$ in air.

Scheme-1: The Synthetic route for the formation of PF-resins
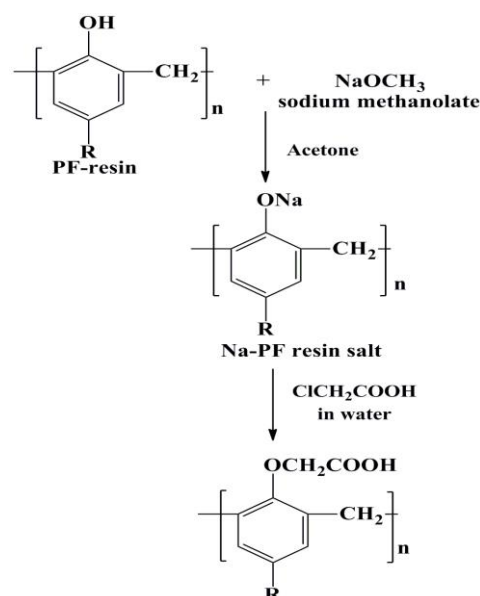
CMPF 1 to 4, Where R = H, CH_3, i-C_3H_8, t-C_4H_{10}

Table 2:Structure of CMPF resins

Polymer sample	Designation	Structure of CMPF resin	Yield
1	CMPF-1		80%
2	CMPF-2		82%
3	CMPF-3		84%
4	CMPF-4		83%

Table3: Non-aqueous conductometric titration and Number average molecular weight $\overline{Mn}$ by VPO

Resins	Non-aqueous conductometric titration mmol of –COOH /100gm	$\overline{Mn}$ by VPO in DMF at $70^o \pm 0.1^oC$. ± 20
CMPF-1	26.82	650
CMPF-2	24.72	720
CMPF-3	21.46	800
CMPF-4	20.01	850

Viscosity Measurement: The relative, specific and reduced viscosity of the CMPF resin solutions from the flow times of solutions was measure by using the Ubbelohde capillary viscometer. The viscosity measurements were carried out at a constant temperature of $30^o \pm 0.3^oC$. 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 [ɳ] is determined.

Results and Discussion:

All the four resins i.e. CMPF 1 to 4 were in form of amorphous power. The non-aquesconductometric titrations of all the resins require mmoles of sodium methanolate per 100g sample for neutralization. These are showing **Table-3**. The data suggest that the value is consistent with the structure. The number average molecular weight $\overline{Mn}$ of all the four resins is in the rage of 650 to 850 depending of the nature of polymer. The IR spectra of all the resins are almost identical in shape and intensity of bands. Only discernible band are $1720cm^{-1}$ is responsible to –COOH group. This also supported by thermogravimetric analysis (TGA). The TGA at all the resins gives the two step degradation as shown in **Figure 1**. The I[st] step degradation is mainly due to decarboxylation. The weight loss at 1st step degradation is almost agreed with theoretical weight loss (Typical figure-1 given). All these facts suggest the structure of resins shown in **Table-2**.

The reduced viscosity of the CMPF resin solution in to the DMF solvent is shown in **Figure 2 (Table 4) as** the function of polymer concentration. It is seen from the **Figure 2** 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 [17,18].
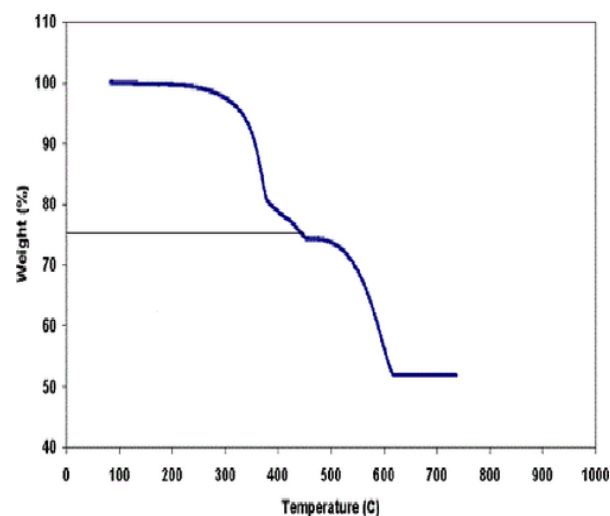
Figure 1. TGA of CMPF 1 resin
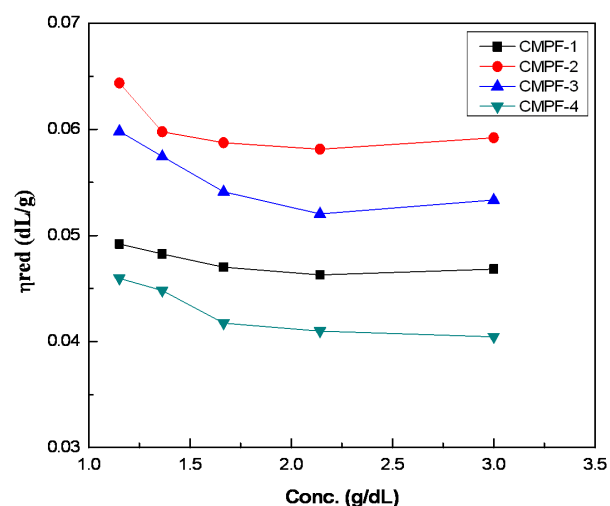
Figure 2. Reduced Viscosity vs Concentration of CMPF resins using DMF

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 cause 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 interactions [20].
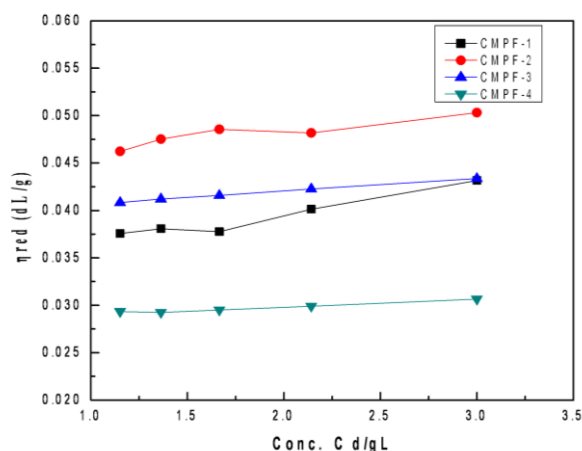
Figure 3: Reduced Viscosity vs Concentration of CMPF resins using DMF-water-KBr (80:20:1%)

Figure 3 (Table 5) shows the Reduced viscosity as a function of polymer concentration in the presence of DMF-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 changes [21]. It is seen from **Figure 3** that there is not electrolyte effect and viscosity does not increase with decreasing polymer concentration, which is in contrast with salt-free solution.

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, (i) 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. (ii) 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 salvation or protection. This situation is created by increasing the solvent power of the solvent e.g. by using a mixture like DMF – water mixture as solvent in place of a pure solvent.
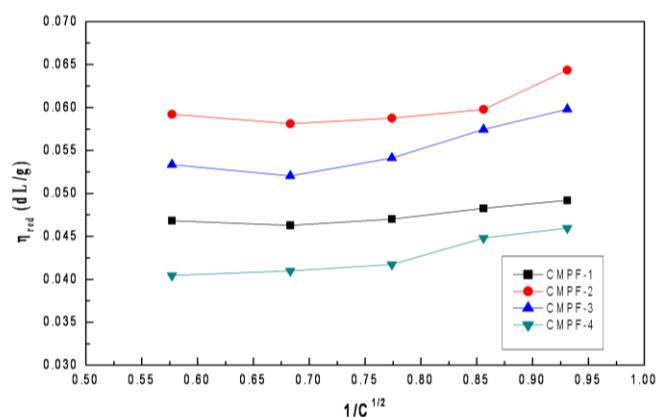

Figure 4: Reduced Viscosity vs $1/C^{1/2}$ of CMPF resins using DMF

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 6**. The plots are shown in **Figure 4**; this was indicated that the plots were linear. From the plots, values of intercept [η] and K were appraised. These constants are presented in table 6. 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, no significance can be attached to the definition of the intercept which follows from the equation.

Conclusion:

The intrinsic viscosity has been determined by extrapolating the reduced viscosity to zero concentration. The effects of solvent DMF, solvent-water, and solvent-water-KBr on viscosity have been investigated. It was shown that the reduced viscosity of DMF using solution of CMPF resins 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 4: Reduce viscosity of solution of CMPF resin 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**
CMPF-1	0.04681	0.04628	0.04700	0.04825	0.04919
CMPF-2	0.05920	0.05812	0.05875	0.05977	0.06436
CMPF-3	0.05335	0.05204	0.05412	0.05744	0.05981
CMPF-4	0.04045	0.04097	0.04173	0.04480	0.04596

Table5: Reduce viscosity of solution of CMPF resin using DMF-water-KBr (80:20:1%)

Polymer Samples	Reduced Viscosity (η_{red}dL/g) at concentration, (C g/dL)					Intrinsic Viscosity $[\eta]x10^2$	Slop of linear plot $K x10^3$
	3.000	**2.142**	**1.666**	**1.363**	**1.152**		
CMPF-1	0.04316	0.04014	0.03777	0.03806	0.03758	3.35	2.83
CMPF-2	0.05030	0.04817	0.04856	0.04751	0.04622	4.47	1.88
CMPF-3	0.04337	0.04227	0.04158	0.04120	0.04083	3.93	1.36
CMPF-4	0.03064	0.02991	0.02949	0.02924	0.02933	2.83	0.76

Table 6: Reduce viscosity of solution of CMPF resin using DMF

Polymer Samples	Reduced Viscosity (η_{red}dL/g) vs $1/C^{1/2}$					Intrinsic Viscosity $[\eta]x10^2$
	0.577	**0.683**	**0.774**	**0.856**	**0.931**	
CMPF-1	0.04681	0.04628	0.04700	0.04825	0.04919	4.19
CMPF-2	0.05920	0.05812	0.05875	0.05977	0.06436	5.03
CMPF-3	0.05335	0.05204	0.05412	0.05744	0.05981	4.00
CMPF-4	0.04045	0.04097	0.04173	0.04480	0.04596	3.02

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