An eco-friendly synthesis, characterization, morphology and chelation ion-exchange properties of a resin

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ABSTRACT

2, 2-dihydroxy biphenyl-thiourea-formaldehyde (2, 2-DHBTF) terpolymer resin was synthesized by an eco-friendly technique in dimethyl formamide medium. The resin was characterized by elemental analysis, UV-Visible, FTIR, ^{1}H NMR, ^{13}C-NMR and viscometric measurement. The surface morphology of the terpolymer resin was established by scanning Electron Microscopy. The number average molecular weight was determined by non-aqueous conductometric titration. One of the important applications of these types of polymer is their capability to act as chelating ion-exchanger. The chelation ion-exchange properties of the terpolymer showed a powerful adsorption towards specific metal ions like Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+}. A batch equilibrium method was adopted to study the selectivity of the metal ion uptake involving the measurement of the distribution of the given metal ion between the polymer sample and a solution containing the metal ion over a wide range of concentrations and pH of different electrolytes.

Introduction

Many copolymers with reactive groups are now being synthesized, tested and used not only for the macromolecular properties but also for the properties of functional groups. These functional groups provide an approach to a subsequent modification of the copolymers for specific end application [1]. In recent years, some comprehensive work has been published on functional monomers and their copolymers [2,3]. Liu and co-workers [4] studied the interaction of heavy metal ions and chelating ion-exchange resin containing 8-hydroxyquinoline (8-HQ). The resin has good selectivity to exchangeable adsorption of heavy metal ions indicating Cu (II), Hg (II), Pb (II) and Mg (II) under pH 5.0 and also suggested that the chelating ion-exchange resin containing 8-HQ could be used to enrich heavy metals in water and their analysis. Salih Bekir [5] has prepared modified 1,4,8,11-tetraazocyclotridecane (cyclam) and with an AIBN initiator polymerized the modified cyclam. Cyclam containing polymer in bulk structure was removed from the suspension by filtration after washing and drying. The polymeric materials were used for transition metal ion adsorption and desorption of selected ions Cu (II), Ni (II), Co (II), Cd (II), and Pb (II) from aqueous media containing different amounts of these metal ions at different pH values. The adsorption rates were high and the adsorption equilibrium was reached in about 30 min. The affinity order of the transition metal ions was Cu (II) > Ni (II) > Co (II) > Cd (II) > Pb for competitive adsorption. Gurnule and co-workeres [6] have prepared 8-hydroxyquinoline - melamine - formaldehyde (8-HQMF) resin. The chelating ion-exchange properties of this were studied for Cu^{+2}, Ni^{+2}, Co^{+2}, Zn^{+2}, Cd^{+2}, Fe^{+3} and Pb^{+2} ions. A batch equilibrium method was used to study the selectivity of metal ion uptake by measuring the distribution of a metal ion between the resin sample and solution containing the metal ion. The study was carried out at different pH ranges and in medium of different ionic strengths. The copolymer showed higher selectivity for Fe (III), Cu (II) and Ni (II) ions than Co (II), Zn (II), Cd (II) and Pb (II) ions.

Recently, shah et al reported the chelating ability of the resin synthesized by a microwave irradiation technique involving salicylic acid and formaldehyde [7].

The present study deals with the synthesis and characerisation of 2, 2-dihydroxy biphenyl-thiourea-formaldehyde terpolymer resin by polycondensation, an ecofriendly synthyesis in dimethyl formamide medium (DMF), for the first time. The synthesized terpolymer was characterized by elemental analysis, UV-Visible, FTIR, ^{1}H NMR, ^{13}C-NMR and viscosity measurement. Further the chelation ion exchange property of the 2, 2-dihydroxy biphenyl-thiourea-formaldehyde terpolymer resin was also reported for specific metal ions.

Experimental

Materials:

The Chemicals used were all of A. R. or chemically pure grade.

Synthesis of 2, 2-DHBTF terpolymer resin:

A mixture of 2, 2-dihydroxy biphenyl (1.862 gm, 0.1 mole), thiourea (0.76 gm, 0.1 mole), formaldehyde (7.5 ml, 0.2 mole) and 2M hydrochloric acid (200 ml) was taken in a RB flask fitted with a water condenser and heated in an oil bath at 126 ± 2 ^{0}C for 6 hours (Scheme 1) with occasional shaking [8-12]. The temperature of electrically heated oil bath was controlled with the help of dimmerstat. The resinous solid product obtained was immediately removed from the flask as soon as the reaction period was over and then purified.

The resinous product so obtained was repeatedly washed with cold distilled water dried in an air and powdered with the help of agate mortar and pestle. The powder was washed many times with hot water to remove unreacted monomers. The air

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dried powder then extracted with diethyl ether and then with petroleum ether to remove unreacted monomers which might be present along with 2, 2-DHBTF terpolymer. It was further purified by dissolving in 8% sodium hydroxide solution, filtered and reprecipitated by gradual dropwise addition of ice cold 1:1 (v/v) concentrated hydrochloric acid/distilled water with constant and rapid stirring to avoid lump formation. The process of reprecipitation was repeated thrice. The 2, 2-DHBTF terpolymer resin so obtained was filtered, washed several times with hot water, dried in air, powdered and kept in vacuum desiccator over silica gel. The reaction taking place is as follows.
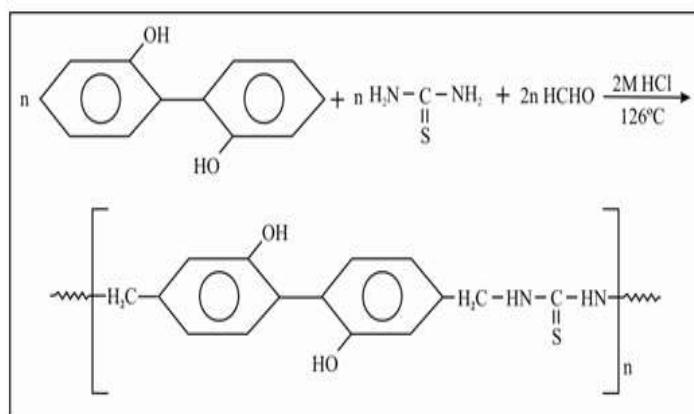
Scheme 1: Preparation of 2, 2-DHBTF Terpolymer

Characterisation
Elemental analysis
The carbon, hydrogen and nitrogen of the terpolymer resin were done by microestimation technique by using Perkin Elmer 2400 Elemental analyzer at Sophisticated Analytical Instrument Facility, Punjab University Chandigarh.

U-V Visible spectra
UV-Visible spectra of the terpolymer resin was recorded at room temperature in dimethyl formamide (spectroscopic grade) in 850 to 200 nm range by using UV 240 shimadzu automatic recording double beam spectrophotometer fitted with an automatic pen chart recorder at Sophisticated Analytical Instrument Facility, Punjab University, Chandigarh [13].

Infrared Spectra
Infra red spectra of the newly synthesized terpolymer resin [14] were scanned at Sophisticated Analytical Instrument Facility, Chandigarh in KBr pellet on Perkin Elmer Model 577 IR spectrophotometer in the region 4000-200 cm^{-1}.

NMR Spectra
NMR spectra of the new terpolymer resin were scanned on 90 MHz for ^{1}H using Bruker advance II 400 NMR Spectrometer Sophisticated Analytical Instrument Facility, Punjab University Chandigarh. For Nuclear magnetic resonance studies of non-aqueous solution, the most reference compound is tetramethyl silane $(CH_3)_4Si$, which is magnetically and electrically isotropic, chemically reasonably inert and non-associating with any common compound. When the high field absorbing tetramethyl silane is used as reference, most (δ) values are negative. The chemical shifts are solvent dependent [15].

Molecular weight determination
The molecular weight of terpolymer resin has been measured by conductometric titration in non-aqueous media [16] against proper standard results was used in the determination of molecular weight of polymer containing phenolic - OH group or -COOH group in the repeat units. Conductometric titration in non-aqueous media has proved to be a simple method for estimation of number average molecular weight of polymer. A Philips conductivity bridge was used to measure the resistance of the solution.

A weighed amount of polymer sample (25 mg.) was dissolved in 25 ml distilled N, N-dimethyl sulphoxide in a beaker. The solution was left aside for 12 hours. The conductivity cell was then dipped in this solution to measure its resistance. Standard ethanolic potassium hydroxide was used as titrant. The titrant was added to the polymer solution in lots of 0.1 ml till the total amount of titrant was 2.0 ml. till the appropriate stage of titration was carried out far beyond the stage of equivalence.

The titrations were carried out at room temperature. Two or three minutes were allowed to lapse after each addition of the titrant, before conductance reading was noted. This secured uniform temperature in the measurement. The conductometric titration was carried out to the stage of equivalence i.e. a stage when all the phenolic hydroxyl groups or –COOH groups were neutralized by the titrant base. Beyond the stage of equivalence, conductance continued to increase steadily. This observation allowed decision of the polymer chains. The amounts of ethanolic potassium hydroxide added in milliequivalents of base (KOH) required for neutralization of 100gm of sample was made.

Inspection of such a plot revealed that was several steps in the plots. From the plots, the amount of the titrant added up to the first break was noted. This was the smallest of all the breaks. It was assumed that this corresponded to a stage in titration when on an average one - COOH group or one - OH group of each polymer chain was neutralized. The titration curves indicate a sharp stepwise increase in the conductance, till the stage of neutralization of all the - COOH groups or - OH groups as the case may be reached. Beyond this stage there was a continuous increase in conductance. The degree of polymerization $\overline{DP}$ of the polymer sample was obtained from the ratio of total milliequivalents of base required to reach the final stage of neutralization to the milliequivalents corresponding to the first break in the plots [16, 17].

$$\overline{DP} = \frac{\text{Total meq. of base required for complete neutralisation}}{\text{meq. of base for smallest interval}} \qquad ----------\text{I}$$

$$\overline{Mn} = \overline{DP} \times \text{Repeat unit weight} \qquad ----------\text{II}$$

Viscosity measurements
The information about the molecular weight of the polymer samples estimated by conductometric method would be placed on a more firm basis if the results are supported by the similar information furnished by other methods. Such information is provided by the results of viscometric study of the polymers.

Viscosity is a unique property that a dilute polymer solution has much higher viscosity than that of the pure solvent. This large difference in viscosity and various functions derived are usually measured to produce information regarding the nature of the micro-structure of the resins under study. It would be note worthy and proper to define viscosity functions which are being estimated for this purpose.

Various definitions of Viscosity:

Relative Viscosity:- The ratio of the solution (η) to viscosity of the solvent (η_0)

$$\eta_{rel} = \frac{\eta}{\eta_o} \quad \text{-----------------------III}$$

Specific Viscosity :- This function has been derived from relative viscosity

$$\eta_{sp} = \eta_r - 1 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{IV}$$

Reduced Viscosity :- The ratio of specific viscosity (η_{sp}) and concentration of polymer sample (C) is known as reduced viscosity.

$$\eta_{red} = \eta_{sp} / C \quad \text{--------------------------V}$$

Intrinsic Viscosity :- The measurement of reduced viscosity of solutions of different concentrations and extrapolating of zero concentration gives a characteristic parameter of polymer known as " Intrinsic Viscosity" denoted by [η].

$$\eta_{int} = \lim_{c \to o} \left[\frac{\eta_{sp}}{C} \right] \quad \text{--------------------VI}$$

The relation between intrinsic viscosity and measured average molecular weight $(\overline{Mn})$ of the polymer sample is denoted as -

$$\eta_{int} = K\overline{M}^{\alpha} \quad \text{-------------------------------VII}$$

Where, K and α are constants and $\overline{Mn}$ gives average molecular weights of resins. This relation is known as Mark Houwnik equation and it is applicable to nearly straight chain polymers.

Huggin's equation

The relation between reduced viscosity and concentration are expressed by Huggin [18] as

$$\eta_{sp}/C = [\eta] + K_1[\eta]^2 C \quad \text{------------------VIII}$$

where, K_1 is Huggin's constant

Kraemmer's Equation

The relation between inherent viscosity $\ln\eta_r/C$ and concentration is expressed by Kraemmer [19] as,

$$\ln\eta_r/C = [\eta] - K_2[\eta]^2 C \quad \text{------------------IX}$$

where, K_2 = Kraemmer's constant

Thus intrinsic viscosity is computed by plotting η_{sp}/C against C or $\ln\eta_r/C$ against C and extrapolating the linear plot to zero concentration. The intercept of these graphs gives the value of intrinsic viscosity. The results obtained by application of viscosity measurements of polymer have been used to decide the trend in the molecular mass of terpolymer samples. The intrinsic viscosity of all terpolymer resins were estimated in DMSO at 30 ^{0}C using Tuan-Fuoss Viscometer fabricated in our laboratory [20].

A. For the determination of Metal Ion Uptake in the presence of electrolytes of different Concentration:

The following procedure was applied in order to study the effect of the nature of the various electrolytes and their concentration on the amount of the metal ions taken up by the terpolymer resin sample.

25 mg of the finely powdered terpolymer sample was suspended in an electrolyte solution (25 ml) of known concentration. The pH of the solution was adjusted to the required value by using either 0.1M HNO_3 or 0.1M NaOH. The suspension was stirred for a period of 24 hours at room temperature. To this suspension 2 ml of a 0.1M solution of the metal ion was added and the pH was adjusted to the required value. The mixture was again stirred at 27 ^{0}C for 24 hours and filtered. The solid was washed and the filtrate along with the washing was estimated for the metal ion content by titration against standard EDTA using appropriate buffer and suitable indicator. A blank experiment was also carried out in the same manner without adding the polymer sample. The blank solution was again estimated for the metal ion content. The amount of metal ion taken up by the terpolymer in the presence of the given electrolyte of known concentration is determined from the difference between the blank reading and the reading in the actual experiment[21]. The experiment was repeated in the presence of several electrolytes of known concentration with eight different metal ions viz. Fe (III), Co (II), Ni (II), Cu (II), Zn (II).

B. For the evaluation of rate of Metal Ion Uptake:

To estimate the time required to reach the state of equilibrium under the given experimental conditions, a series of experiments of the type described above were carried out, in which the metal ion taken up by the terpolymer resin was estimated from time to time at room temperature (300K) in presence of 25 ml of 1M $NaNO_3$ solution. It is assumed that under the given conditions, the state of equilibrium is established within 24 hours. The rate of Metal ion uptake is expressed as percentage of the amount of metal ions taken up after a certain time related to that in the state of equilibrium [21-23].

C. For the evaluation of the distribution of metal ions at different pH:

The distribution of each one of the six metal ions viz. Fe(III), Co(II), Ni(II), Cu(II), Zn(II) between polymer phase was estimated at 300K and in presence of a 1M $NaNO_3$ solution [21-23]. The experiments were carried out as described above in the pH range 2 to 6.5. The distribution coefficient (D) was calculated by the relationship:

$$*D = \frac{\text{Weight (in mg) of metal ion taken up by 1g of polymer}}{\text{Weight (in mg) of metal ion present in 1 ml of solution}}$$

Results and Discussion

2, 2-DHBTF terpolymer resin is light pink in colour. This purified terpolymer resin is found to be soluble in N,N-dimethyl formamide, Dimethyl sulphoxide, aqueous sodium hydroxide solution.

1. Elemental analysis

2, 2-DHBTF terpolymer resin was analyzed for the percentage of carbon, hydrogen and nitrogen at SAIF Chandigarh. The results are presented in table 1. From the Table 1, it is found that the values of the % elements determined are in good agreement with the calculated values. The elemental analysis data suggest the empirical formula and the empirical formula weight for the repeating unit of 2, 2-DHBTF terpolymer resin as given in Table 1.

2. UV-Visible Spectra

UV-Visible spectra of 2, 2-DHBTF terpolymer resin in pure dimethyl formamide were recorded in the region 200 to 850 nm. The spectra of all the terpolymer exhibit two absorption maxima in the region 220-240 nm and 270-300 nm The intense band at 232 nm is due to ($\pi \to \pi^*$) allowed transition of biphenyl moiety which readly attains coplanarity. The intense band at 286 nm is due to ($n \to \pi^*$) forbidden transition in saturated aliphatic carbonyl compounds [18, 24].

The bathochromic shift from the basic value viz. 232 nm and 286 nm respectively may be due to combined effect of conjugation and phenolic hydroxyl group (auxochrome) [19, 24, 25].

Table 1: Synthesis and Physical Data of Terpolymer

Reactants	2,2 -dihydroxy biphenyl "DHB" (mole)		0.1
	Thiourea "T" (mole)		0.1
	Formaldehyde "F" (mole)		0.1
Catalyst	2M HCl (aq.) (ml)		200
Reflux Temp ± 2K			399
Resin abbreviation			2,2-DHBTF
Molar ratio of Reactants			(1:1:2)
Yield (%)			69
Melting Point of resin (K)			723
Elemental Analysis (%)	C%	Obs.	60.41
		Cal.	62.94
	H%	Obs.	4.89
		Cal.	4.90
	N%	Obs.	8.47
		Cal.	9.79
Empirical formula of repeating unit			$C_{15}H_{14}N_2O_2S_1$
Empirical formula weight			286

Table 3: Viscometric data for 2,2-DHBTF Terpolymer Resin

Solvent : DMSO

Temperature : 300 ± 0.1 K

Efflux time of pure solvent (t_0) = 56 sec.

Polymer Concent-ration	Efflux time (t)	Relative viscosity $\eta_r = t/t_0$	Specific viscosity $\eta_{sp} = t-t/to$	Reduced Viscosity $\eta_{red} = \eta_{sp}/C$	$ln\eta_r$	Inherent Viscosity $ln\eta_r/C$	Intrinsic viscosity [η] (dl.g⁻¹)	
							Huggin's relations	Kraemmer's relations
0.5	57.40	1.025	0.025	0.050	0.0246	0.0493		
1.0	58.58	1.046	0.046	0.046	0.0449	0.0449		
1.5	59.50	1.0625	0.062	0.041	0.0606	0.0404	0.056	0.056
2.0	60.10	1.0732	0.073	0.036	0.0706	0.0353		
2.5	60.48	1.0800	0.080	0.032	0.0769	0.0307		
3.0	60.52	1.0807	0.080	0.026	0.0776	0.0258		

Table 5: Comparison of the rates of Metal Ion Uptake**

Metal ion	Terpolymer Resin sample	Percentage of the amount of metal ion taken up* at different time (in hours)						
		1	2	3	4	5	6	7
1	2	3	4	5	6	7	8	9
Fe(III)		65	84	97	-	-	-	-
Cu(II)		44	54	68	81	94	-	-
Ni(II)	2,2-DHBTF	35	49	62	81	94	-	-
Co(II)		36	51	64	78	92	-	-
Zn(II)		32	47	65	81	92	-	-

** Metal ion concentration = 0.1 mole/litre Volume = 2 ml

$NaNO_3$ concentration = 1.0 mole/litre, Volume = 25 ml

*Related to the amount of metal ion in the state of equibrium (100%)

Temperature = 300 K

Table 4: Evaluation of the influence of 2,2-DHBTF different electrolytes on the uptake of several metal ions*

Metal ion	Electrolyte (mole/l)	Weight of metal ion (in mg) taken up in presence of**			
		NaClO$_4$	NaCl	NaNO$_3$	Na$_2$SO$_4$
Fe(III)	0.01	1.02	0.29	1.06	2.36
	0.05	1.99	0.75	1.53	1.39
	0.10	2.27	1.58	1.86	1.29
	0.50	2.61	2.03	2.03	0.81
	1.00	2.98	2.75	2.44	0.25
Cu(II)	0.01	1.68	1.08	1.16	3.38
	0.05	2.18	2.08	1.69	2.69
	0.10	2.58	2.54	2.28	1.81
	0.50	3.05	3.19	2.65	0.96
	1.00	4.42	3.47	2.78	0.07
Ni(II)	0.01	1.90	1.23	0.95	2.80
	0.05	2.13	1.65	1.61	2.35
	0.10	2.43	2.54	2.46	1.55
	0.50	2.58	2.98	3.02	0.78
	1.00	3.45	3.58	3.23	0.15
Co(II)	0.01	1.69	1.88	1.90	1.68
	0.05	1.37	1.70	1.09	1.26
	0.10	1.05	1.09	0.92	0.85
	0.50	0.50	0.87	0.53	0.39
	1.00	1.05	0.49	0.37	0.14
Zn(II)	0.01	2.38	2.69	2.89	1.09
	0.05	2.05	2.39	2.58	1.35
	0.10	1.56	0.65	0.82	1.21
	0.50	0.78	0.35	0.56	0.73
	1.00	0.56	0.06	0.19	0.54

* Concentration of metal ion = 0.1 mole per litre
Volume of metal ion solution = 2 ml
**Volume of electrolyte solution = 25 ml
Note: 1) pH = 4.5 for Cu(II) and Ni(II) 2) Temperature = 300 K
= 2.75 for Fe(III) = 5.0 for Co(II) and Zn(II)

Table 6: Distribution Ratio (D)* of different metal ions as function of pH

Metal ion	Terpolymer Resin sample	Percentage of the amount of metal ion taken up* at different time (in hours)									
		1.5	1.75	2.0	2.5	3.0	3.5	4.0	5.0	6.0	6.5
1	2	3	4	5	6	7	8	9	10	11	12
Fe(III)		11.2	150.5	266.8	400.1	-	-	-	-	-	-
Cu(II)		-	-	-	41.0	91.6	174.3	321.6	1152.0	1560.2	1654.2
Ni(II)	2,2-DHBTF	-	-	-	33.1	89.8	130.0	300.2	452.3	1006.2	1059.2
Co(II)		-	-	-	26.9	39.5	90.2	105.8	182.6	251.3	265.4
Zn(II)		-	-	-	26.3	35.3	50.2	86.5	116.5	231.2	256.3

$$ *D = \frac{\text{Weight (in mg) of metal ion taken up by 1g of polymer}}{\text{Weight (in mg) of metal ion present in 1 ml of solution}} $$

Metal ion concentration = 0.1 mole/lire, Volume = 2 ml   Time = 24 hour (equilibrium state)
Concentration of NaNO$_3$ = 1.0 mole/litre, Volume = 25 ml   Error = ± 3.0 %, Temperature = 300 K

3. Infra-red Spectra

The IR spectra revealed that this resin give rise to nearly similar pattern of spectra. A broad band appeared in the region 3600-3375 cm^{-1} may be assigned to the stretching vibrations of phenolic hydroxyl groups exhibiting intermolecular hydrogen bonding with carbonyl group of different polymeric chain i.e. -OH phenolic intermolecular polymeric association [18, 26-28]. The broad band at 2925-3375 cm^{-1} is assignable to –NH-stretching vibrations of the urea moiety in terpolymer respectively [26-28]. The sharp bands obtained at 752, 1279, and 1335 cm^{-1} suggest the presence of methylene bridges in the polymer chain. The sharp peaks at 1603 cm^{-1} and 1493 cm^{-1} indicate aromatic skeletal ring breathing modes. The absorption bands at 1220 cm^{-1} and 1075 cm^{-1} recognize 2, 4-disubstituted phenyl ring [18, 26-28].

4. NMR Spectra

Proton NMR spectra of terpolymer resin show a multiplet signal (unsymmetrical pattern) in region 6.6 to 7.6 (δ) ppm which is due to aromatic protons[27]. A broad signal at 9 (δ) ppm shows intramolecular hydrogen bonding of –NH-CS- group or intermediate proton exchange reaction of both phenolic –OH group [29]. A weak signal at 4.4-4.6 (δ) ppm may be due to protons of –NH- bridges [19, 29]. A signal at 3.7 to 3.9 (δ) ppm may be assigned to methylene protons of Ar-CH$_2$-N moiety.

5. Molecular Weight Determination by Conductometric Titration Method

The number average molecular weight of the newly synthesized 2, 2-DHBTF-terpolymer resin has been determined by conductometric titration method in non-aqueous solvent (DMSO). The conductometric titration was carried out in DMSO using standard potassium hydroxide (0.05M) in absolute ethanol as a titrant. The details of the non-aqueous conductometric titration are presented in Table 2. Careful examination of the plot of the titration curve clearly shows that there are several breaks before the complete neutralization of all phenolic hydroxyl groups [29]. The first break in the plot was the smallest of all the breaks. It was assumed that this corresponds to a stage in titration when on average one phenolic hydroxyl group of each chain was neutralized. Examination of conductometric curve reveals that the size of most of the breaks was nearly equal or was whole number multiple of the size of the first break. The experimental data indicate a sharp stepwise increase in conductance till the stage of complete neutralization of all the phenolic hydroxyl groups. Once the neutralization state is achieved, there is continuous steady increase in the value of the conductance.

The amount of standard ethanoic KOH added was transformed in to milliequivalents required for 100g of terpolymer resin and plots against specific conductance. The degree of polymerization $(\overline{DP})$ and hence the number average molecular weight $(\overline{Mn})$ of 2, 2-DHBTF terpolymer have been determined using the formula.

$$\overline{DP} = \frac{\text{Total meq. of base required for complete neutralisation}}{\text{meq. of base for smallest interval}} \quad \text{----------- I}$$

$$\overline{Mn} = \overline{DP} \times \text{Repeat unit weight} \quad \text{----------- II}$$

Thus the degree of polymerization $(\overline{DP})$ and the number average molecular weight $(\overline{Mn})$ was evaluated from the conductometric titration curve and presented in Table 2.

Table 2: Number Average molecular weight data of 2, 2-DHBTF Terpolymer resin by conductometric titration

First stage of neutralization (meq/100 gm of terpolymer)	Final stage of neutralization (meq/100 gm of terpolymer)	Degree of Polymerisation $(\overline{DP})$	Number average molecular weight $(\overline{Mn})$
56	950	16.96	4850

6. Viscosity Measurements

Viscosity measurement of the 2, 2-DHBTF terpolymer resin was carried out in freshly triple distilled dimethyl sulphoxide at 303 K. The details of the experiments and and calculations are furnished in Table 3 and plots for [η]$_{int.}$ determination are presented in Fig. 4. The viscometric measurements were carried out at six different concentrations ranging from 3.0 to 0.5%. The reduced viscosity of the terpolymer sample was calculated by the formula η$_{sp}$/C. Intrisic viscosity [η]$_{int.}$ was determined by the following Huggin's [18] and Krammer's [19] relations.

The relation between reduced viscosity and concentration are expressed by Huggin as,

$$\eta_{sp}/C = [\eta] + K_1[\eta]^2 C$$

The relation between inherent viscosity lnη$_r$/C and concentration is expressed by Kraemmer as,

$$\ln\eta_r/C = [\eta] - K_2[\eta]^2 C$$

In accordance with the above relations of η$_{sp}$/C and lnη$_r$/C were found to be linear. The values of intrinsic viscosity were calculated from the intercepts on the axis of viscosity function of both the plots. Therefore, the values of [η]$_{int}$ obtained from both the plots are in good agreement.

The results of viscometric study exhibit the following trend-
I. The plots of η$_{sp}$/C Vs C and lnη$_r$/C Vs C are linear (Fig 1).
II. 2, 2-DHBTF resin having higher molecular weight has higher intrinsic viscosity (Table 3).
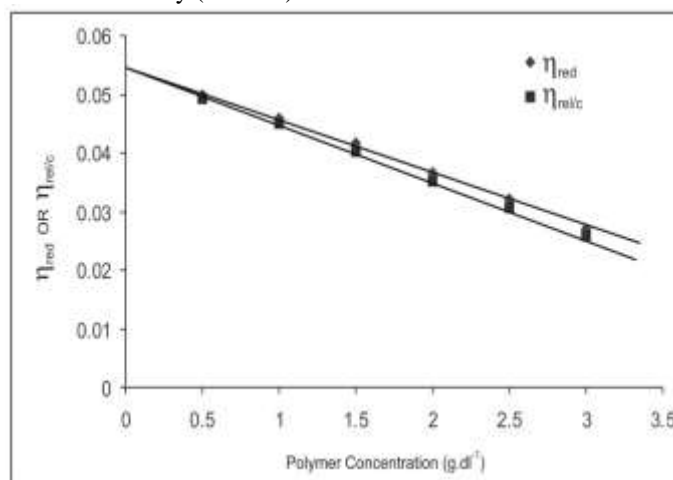

Fig. 1. Viscometric plots of 2,2-DHBTF Terpolymer Resin

2, 2-DHBTF TERPOLYMER RESINS

The results of the batch equilibrium study carried out with 2, 2-DHBTF terpolymer resin sample are presented in Table 4-6. From his study, carried out with five metal ions under limited variation of experimental conditions, certain generalizations may be made about the behavior of 2, 2-DHBTF resin sample.

1. Influence of electrolytes on the Metal Ion Uptake

The data presented in Table 4 reveal that the amount of metal ions taken up by a given amount of terpolymer resin depends on the nature and concentration of the electrolyte present in the solution. In presence of perchlorate, chloride and nitrate ions, the amount of Fe(III), Ni(II), Cu(II) ions taken up by the terpolymer sample increases with increasing concentration of electrolyte, whereas in presence of sulphate ions the amount of the above mentioned ions taken up by the terpolymer sample decreases with increasing concentration of electrolyte [21-23]. Moreover the amount of Co(II), Zn(II) ions taken up by the terpolymer samples decreases with increasing concentration of the chloride, nitrate, perchlorate and sulphate ions. This observation can be explained on the basis of formation constsnt data of the complexes with Co^{2+}, Cu^{2+}, Ni^{2+}, Fe^{3+} and Zn^{2+} metal cations. This type of trend has also been observed by other investigators in this field [21-23].

It has been noticed that a lower pH was not suitable when concentrated electrolytes were used. It was also observed that generally the metal ion adsorption by the terpolymer resin sample is much better in presence of 1M perchlorate solution.

2. Evaluation of the Rates of Metal uptake

The rates of metal ion adsorption by 2, 2-DHBTF terpolymer resin sample were measured for Fe (III), Ni (II), Cu (II), Co (II) and Zn (II) ions in order to know the time required to reach the equilibrium. The term "Rate" refers to the change in the concentration of the metal ions in the aqueous solution with time which are in contact with the terpolymer sample. The experimental results which are presented in table 8 show the dependence of the rate of metal ion uptake on the nature of the metal ions. These results indicate that the time taken for the uptake of the different metal ion under given conditions. Careful examination of the experimental data which are tabulated in Table 5 show that Fe (III) ions require time of 3 hours for the establishment of the equilibrium Cu(II), Ni(II), Co(II) and Zn(II) ions require about 5 hours. The experimental results reveal that the rate of metal ion uptake follows the order: Fe > Cu > Ni > Co > Zn.

3. Distribution Ratios of Metal Ions at Different pH

Table 6 shows the experimental results of the effect of pH on the amount of metal ion distributed between two phases. The data presented in table 9 indicate that the relative amount of metal ions taken up by the terpolymer sample at equilibrium, increases with the increase in pH.

The study was carried out only up to pH 6.5 in order to prevent hydrolysis of the metal ions at higher pH. In case of Fe (III) the highest working pH was 2.5. The results indicate that the selectivity of terpolymer resin sample for Fe (III), Cu(II) and Ni(II) ions is higher than for other metal ions viz. Co(II) and Zn(II) which have shown intermediate selectivity.

The lower distribution ratio of Fe (III) may be attributed to steric hinderance (σ). The other two metal ions viz. Co (II) and Zn (II) have a low distribution ratio (D) over the pH range 3 to 5. This could be attributed to low stability constants.

Thus, in the present study the observed order of distribution ratios of metal ions measured in the range of pH from 3 to 6.5 was found to be Fe(III) > Cu(II)> Ni(II) > Co(II) > Zn(II). The similar trend has been observed by earlier investigators [22].

Thus, the results of such investigations are helpful in selecting the optimum pH for a selective uptake of a particular metal ion from a mixture of different metal ions. For instance, the results suggest the optimum pH 4 for the separation of Zn

(II) using 2, 2-DHBTF terpolymer resin with its distribution ratio 114.7 respectively.

All the experiments were conducted in duplicate and the results were found to be reproducible.

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