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Archives of Applied Science Research, 2012, 4 (3):1395-1402
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Novel polymeric ligand its polymeric metal chelates

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ABSTRACT

Diazonium salt of *p*-toluidine reacted with salicylic acid-formaldehyde polymer afforded a novel ligand PTSA. The ligand PTSA and its metal chelates with Cu(II), Zn(II), Co(II), Fe(III), Mn(II) and Ni(II) metal ions were prepared. The PTSA and its polymeric metal chelates were characterized by elemental analysis, spectral studies, thermogravimetry, diffuse reflectance spectral studies and magnetic susceptibilities. By Batch equilibration method chelation ion-exchanging properties of the polymers were studied. All the samples have also been monitored for microbicidal activity.

Keywords: Azo dyes, salicylic acid-formaldehyde polymer, ion-exchanging properties, antibacterial and antifungal activities.

INTRODUCTION

The effluents from mines and metal industries set up the serious problems in removal of heavy toxic metal ions. The contents of these metals in effluent are almost above the valid limit [1-3]. The contents of this metal can be reduced by treatment of lime, but result is not satisfactorily. Thus ion-exchange technique has been proved very useful in this context. The ion-exchange resin can be use for metal extraction from ore, analytical reagent, and separation of metal ion and deionization of water [4-10]. Most of commercial ion-exchange resins are sulfonated polystyrene-divinylbenzene copolymer [11-12]. The use of complex ion-formation in ion-exchange resin has been prepared to solve the problem [11-12]. The aim of the present work to prepare and study the novel ion-exchange resin based on condensation polymer. Some of the polymer like Salicylic acid-Formaldehyde polymer (SA) and its derivatives are known as ion-exchanges [13-16]. Literature survey reveals that such Salicylic acid-Formaldehyde polymer (SA) type polymers have not been used as azo dye couples. This can afford for novel coloured ion-exchanges with good thermal stability. Hence the present paper comprises the synthesis of novel ion-exchange resin and its ion-exchanging properties. [17-18] Perusal of the literature reveals that such Salicylic acid-Formaldehyde polymer (SA) polymers have not been applied as azo dye coupler. The work describe in the present communication is in connection with the synthesis and characterization of a azo dye based on salicylic acid- Formaldehyde polymer and its polymeric metal chelates. so the proposed present work is in connecting with the polymers based on Salicylic acid-Formaldehyde ligands. The synthetic route is shown in scheme 1.

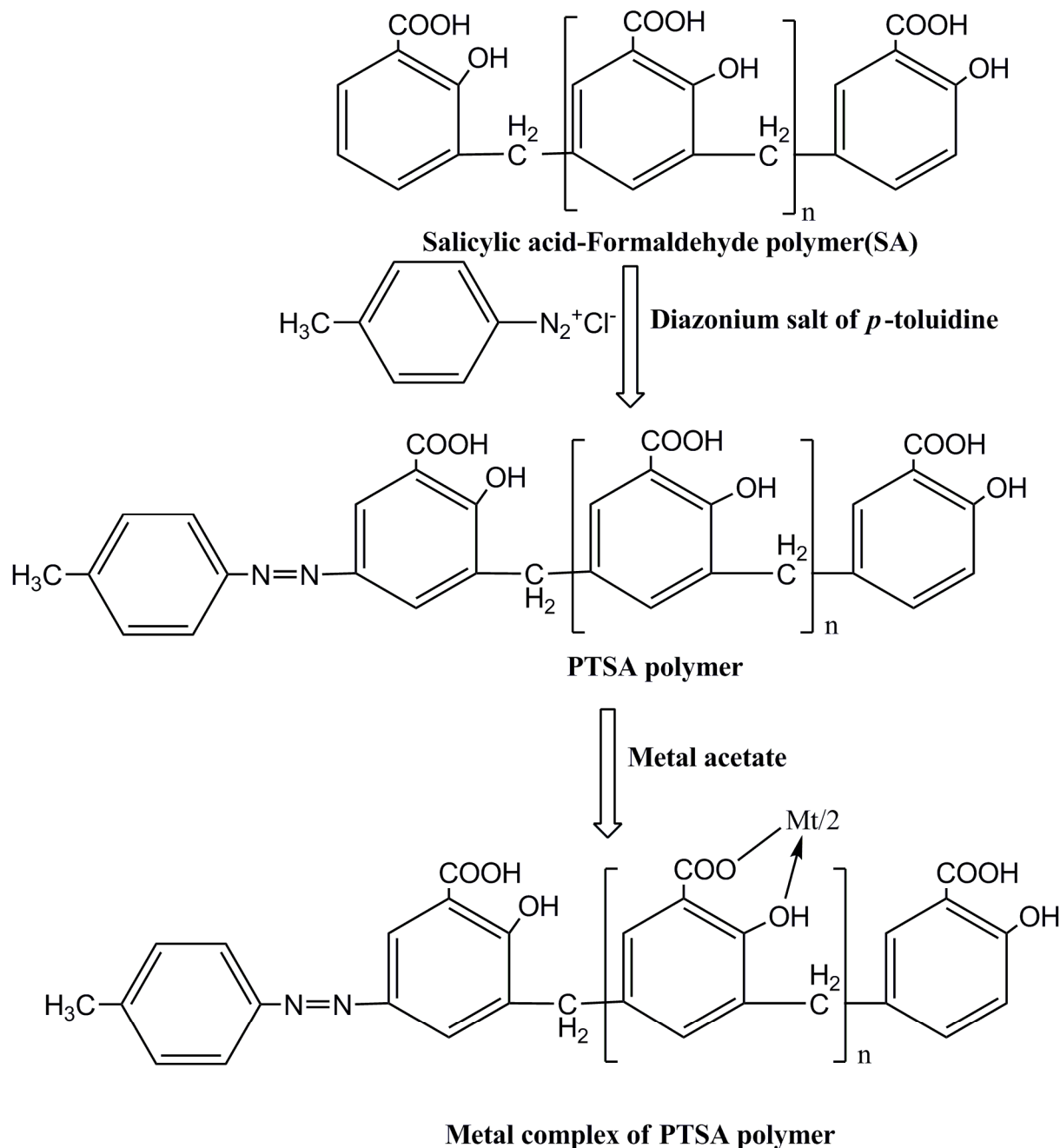
MATERIALS AND METHODS

Materials

Salicylic acid-Formaldehyde polymer (mol.wt.470gm/mole) was prepared by reported method. [19] All the chemicals used were of analytical grade and obtained from local market.

Procedure**Synthesis of azo dyes based on salicylic acid-formaldehyde:****Formation of PTSA**

Preparation of azo coupling of aryl diazonium salts to salicylic acid-formaldehyde (CP-SA): Diazonium salt of p-toluidine solution (0.1mole) was slowly added to an alkaline solution of Salicylic acid-Formaldehyde polymer (SA) (0.1mole) at pH 8.5-9.0 and below 0-5°C. The resultant solution was stirred for 2hr. The dye was precipitated by lowering the pH to 6.0. The precipitated dye (CP-SA) was filtered off, wash with water and air-dried. The yield of PTSA was 79% and m.p.182-184°C (uncorrected). The predicted structure and formation of polymeric ligand is shown in Scheme-1.



Where $\text{Mt}=\text{Cu}^{+2}, \text{Co}^{+2}, \text{Ni}^{+2}, \text{Mn}^{+2}, \text{Zn}^{+2}$ and Fe^{3+}

Scheme-I

Preparation of Polymeric Chelates

The Cu (II), Co(II), Ni(II), Fe(III), Mn (II) and Zn(II) metal chelates of PTSA have been prepared in a similar manner. The procedure is as follow.

To a solution of PTSA (53.3 g, 0.1 mole) in ethanol-acetone (1:1v/v) mixture (150 ml), 0.1N KOH solution was added dropwise with stirring. The pasty precipitates were obtained at neutral pH. These were dissolved by addition of water up to clear solution. It was diluted to 250 ml. by water and was known as stock solution. 25 ml of the stock solution (which contains 0.01 mole CP-SA) was added drop wise to the solution of metal salt (0.005 mole for divalent metal ions and 0.0033 mole for Fe(III) ion) in water at room temperature. Sodium acetate or ammonia was added up to complete precipitation. The precipitates were digested on water bath at 80° C for 2.5 hrs. The digested precipitates of chelates were filtered washed with water and air dried. It was amorphous powder. Yield was almost quantitative. The details are given in Table-1.

MEASUREMENTS

Elemental analysis of PTSA and its polymers were carried out on a C, H, N elemental analyzer (Italy). IR spectra of H₂L and the polymeric chelates were scanned on a Nicolet-760D FTIR spectrophotometer in KBr. The azo group was determined by reported method.[20] The metal content analyses of the polymeric chelates were performed by decomposing a weighed amount of each polymeric chelates followed by EDTA (disodium ethylene diamine tetra acetate) titration as reported in the literature [21]. Magnetic susceptibility measurements of all the polymeric chelates were carried out at room temperature by the Gouy method. Mercury tetrathiocyanatocobaltate (II), Hg[Co(NCS)], was used as a calibrant. Molar Susceptibilities were corrected for diamagnetism of component atoms using Pascal's constant. The diffuse reflectance spectra of the solid polymeric chelates were recorded on a Beckman DK-2A spectrophotometer with a solid reflectance attachment. MgO was employed as the reference compound.

TABLE 1 Analytical and spectral data of the polymeric metal chelates of PTSA (H₂L)

Ligand/ polymers	Empirical Formula	Formula Weight	Analyses %Found(Calculated)				μ_{eff} (B.M.)
			%M	%C	%H	%N	
PTSA	C ₂₈ H ₂₅ N ₂ O ₉	533	-	63.0 (63.03)	4.5 (4.52)	5.0 (5.06)	-
[Cu(PTSA)(H ₂ O) ₂] _n	Cu.C ₅₆ H ₄₈ N ₄ O ₁₈ .2H ₂ O	1163.54	5.4 (5.46)	57.7 (57.75)	4.4 (4.46)	4.8 (4.81)	2.01
[Co(PTSA)(H ₂ O) ₂] _n	Co.C ₅₆ H ₄₈ N ₄ O ₁₈ .2H ₂ O	1158.94	5.0 (5.08)	57.9 (57.98)	4.4 (4.48)	4.8 (4.83)	2.86
[Ni(PTSA)(H ₂ O) ₂] _n	Ni.C ₅₆ H ₄₈ N ₄ O ₁₈ .2H ₂ O	1158.71	5.0 (5.06)	57.9 (57.99)	4.4 (4.48)	4.8 (4.83)	4.05
[Mn(PTSA)(H ₂ O) ₂] _n	Mn.C ₅₆ H ₄₈ N ₄ O ₁₈ .2H ₂ O	1154.94	4.7 (4.75)	58.1 (58.18)	4.4 (4.50)	4.8 (4.84)	4.81
[Fe(PTSA)(H ₂ O) ₃] _n	Fe.C ₈₄ H ₇₂ N ₆ O ₂₇ .3H ₂ O	1706.85	3.2 (3.27)	58.0 (59.05)	4.5 (4.56)	4.9 (4.92)	4.90
[Zn(PTSA)(H ₂ O) ₂] _n	Zn.C ₅₆ H ₄₈ N ₄ O ₁₈ .2H ₂ O	1165.38	5.6 (5.61)	57.6 (57.66)	4.4 (4.46)	4.7 (4.80)	Diamagnetic

Thermogravimetric analysis of PTSA with its metal chelates were carried on DuPont 950 TGA analyzer in air at a heating rate of 20°C/min.

The batch equilibration method was adopted for the ion-exchanging properties [22-23]. The evaluation of the influence of different electrolytes on metal uptake by the polymer, the rate of metal uptake under specified conditions and distribution of various metal ions of different PH values were carried out following the details of the procedures described earlier[22-23].

TABLE 2 Thermo gravimetric analysis polymers of PTSA

Ligand/ polymers	% weight loss at temperature T(°C)					
	100	200	400	500	600	700
PTSA(H ₂ L)	-	19.9	30.2	40.1	45.5	48.1
[CuL(H ₂ O) ₂] _n	2.4	4.5	12.8	42.4	47.6	53.0
[CoL(H ₂ O) ₂] _n	4.5	8.4	16.4	21.8	43.4	59.2
[NiL(H ₂ O) ₂] _n	4.6	8.2	14.6	26.5	45.2	58.9
[MnL(H ₂ O) ₂] _n	4.7	6.2	9.3	15.3	24.6	36.1
[ZnL(H ₂ O) ₂] _n	2.0	3.1	4.4	15.2	23.3	35.2
[FeL(H ₂ O) ₃] _n	2.1	3.3	3.5	14.1	20.4	34.7

Antibacterial activities

Antibacterial activity of PTSA ligand and its polymers were studied against gram-positive bacteria (*Bacillus subtilis* and *staphylococcus aureus*) and gram-negative bacteria (*E.coli* and *salmonella typhi*) at a concentration of 50µg/ml by agar cup plate method. Methanol system was used as control in this method. The area of inhibition of zone measured in mm.

TABLE 3 Antibacterial activities of polymers

Compounds	Zone of Inhibition(mm)			
	Gram +Ve		Gram -Ve	
	<i>Bacillus subtilis</i>	<i>Staphylococcus aureus</i>	<i>Salmonella typhi</i>	<i>E.coli</i>
[CuL(H ₂ O) ₂] _n	62	71	68	70
[CoL(H ₂ O) ₂] _n	66	75	64	71
[NiL(H ₂ O) ₂] _n	64	72	76	84
[MnL(H ₂ O) ₂] _n	63	71	83	83
[ZnL(H ₂ O) ₂] _n	68	66	74	69
[FeL(H ₂ O) ₃] _n	67	63	73	68

Antifungal activities

The fungicidal activity of all the compounds was studied at 1000 ppm concentration in vitro. Plant pathogenic organisms used were *penicillium expansum*, *Nigrospora Sp.*, *Trichothesium Sp.*, and *Rhizopus nigricum*. The antifungal activity of ligand and its polymers was measured on each of these plant pathogenic strains on a potato dextrose agar (PDA) medium. Such a PDA medium contained potato 200gm, dextrose 20gm, agar 20gm and water one liter. Five days old cultures were employed. The compounds to be tested were suspended (1000ppm) in a PDA medium and autoclaved at 120° C for 15 min. at 15atm. pressure. These medium were poured into sterile Petri plates and the organisms were inoculated after cooling the petri plates. The percentage inhibition for fungi was calculated after five days using the formula given below:

$$\text{Percentage of Inhibition} = 100(X-Y) / X$$

Where, X = Area of colony in control plate

Y = Area of colony in test plate

TABLE 4 Antifungal activities of polymers

Compounds	Zone of Inhibition at 1000 ppm (%)			
	<i>Penicillium Expansum</i>	<i>Nigrospora Sp.</i>	<i>Trichothesium Sp.</i>	<i>Rhizopus Nigricum</i>
[CuL(H ₂ O) ₂] _n	77	79	63	62
[CoL(H ₂ O) ₂] _n	68	72	67	76
[NiL(H ₂ O) ₂] _n	76	83	74	75
[MnL(H ₂ O) ₂] _n	75	77	86	80
[ZnL(H ₂ O) ₂] _n	63	78	75	76
[FeL(H ₂ O) ₃] _n	61	75	72	73

RESULTS AND DISCUSSION

The synthesis of the ligand, azo dye based on salicylic acid-formaldehyde (PTSA) has not been reported in the literature. The ligand PTSA was isolated in the form of a pale greenish white powder. It is insoluble organic solvents such as in dioxane, DMSO (dimethyl sulfoxide), DMF. The results of elemental analyses of the PTSA ligand (Table-1) are agreed with those predicted on the basis of formula.

The IR spectrum of PTSA features are a broad band extending from 3450-3160 cm⁻¹ with maximum at 3314 cm⁻¹, attributed to the OH group [24]. The weak bands around 2890 and 2940 cm⁻¹ may be due to asymmetric and symmetric stretching vibrations of methylene groups(-CH₂-). The band at 1680cm⁻¹ due to COOH group. The others bands are at their respective positions.

The polymers derived from PTSA are insoluble in common organic solvents. Hence it is not possible to characterized the polymers by molecular mass using conventional methods like osmometry, viscometry etc. These polymers do not melt up to 360°C.

On the basis of the proposed structure shown in Scheme1, the molecular formula of the PTSA ligand is C₂₈H₂₅N₂O₉, which upon chelation coordinates with two central metal atom at four co-ordination sites and two water molecules. Therefore, the general molecular formula of the resulting polymer is given by [M(PTSA).2H₂O] as shown in scheme-1. This has been confirmed by the results of elemental analyses of all of the five polymers and their parent

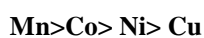
ligand. The data of elemental analyses reported in Table 1 are in agreement with the calculated values of C, H and N based on the above mentioned molecular formula of the parent ligand as well as polymers. Examination of data of the metal content in each compound revealed a 1:2 metal: ligand (M: L) stoichiometry in all of the chelate of divalent metal ions and 1:3 metal: ligand stoichiometry for Fe(III).

Comparison of the IR spectrum of the ligand PTSA and those of the polymers reveals certain characteristic differences. The broad band at 3400-3100 cm^{-1} for PTSA has almost disappeared for the spectra of polymers. However, the weak bands around 3200 cm^{-1} in the spectra of PTSA-Co(II), PTSA-Ni(II), PTSA-Mn(II) indicate the presence of water molecules which may have been strongly absorbed by the polymer sample. The weak band around 1110 cm^{-1} is attributed to the C-O-M stretching frequency [25]. The band at 1430 cm^{-1} in the IR spectrum of PTSA is attributed to the in-plane OH deformation [25]. The band is shifted towards higher frequency in the spectra of the polymers indicating formation of metal-oxygen bond. These features suggest that the structure of the polymer. Magnetic moments (μ_{eff}) of polymeric chelates are given in Table 1.

The diffusion electronic spectrum of PTSA-Cu(II) polymers shows two broad bands around 15,379 cm^{-1} and 22,728 cm^{-1} . The first bands may be due to ${}^2T_{2g} \rightarrow {}^2E_g$ transition, while the second may be due to charge transfer. The first band shows structure suggestion a distorted octahedral structure for the PTSA -Co(II) polymers. The higher value of μ_{eff} of the PTSA -Cu(II) polymer support this view [26,27]. The PTSA -Ni(II) and PTSA -Co(II) polymers give two absorption bands respectively at 17,250 and 23,998 cm^{-1} and at 17,237 and 23728 cm^{-1} which can be assigned respectively to ${}^4T_{1g} \rightarrow {}^2T_{2g}$, ${}^4T_{1g} \rightarrow {}^4T_{1g(P)}$ transitions. These absorption bands and the values of μ_{eff} indicate an octahedral configuration for the PTSA -Ni(II) and PTSA -Co(II) polymers [28,29]. The spectrum of [Mn PTSA (H₂O)₂] show weak bands at 16,479, 17,690 and 23,162 cm^{-1} assigned to the transitions ${}^6A_{1g} \rightarrow {}^4T_{1g}(4G)$, ${}^6A_{1g} \rightarrow {}^4T_{2g}(4G)$ and ${}^6A_{1g} \rightarrow {}^4A_{1g}, 4E_g$ respectively, suggesting an octahedral structure for the [Mn CP-SA(H₂O)₂] polymer [29]. The spectrum of Fe (III) complex has not been adequately characterized. The spectrum comprised the band ground 19019 cm^{-1} and other weak band ground 23011 cm^{-1} . The latter has not very long tail. These may have the transition ${}^6A_{1g} \rightarrow {}^4T_{2g}(4G)$ and ${}^6A_1 \rightarrow {}^4T_1(4G)$. The high intensities of the bands suggests that they might be charge transfer in origin μ_{eff} is found to be lower than normal range. In the absence of low temperature moments it is difficult to give any significance. As the spectrum of the [Zn PTSA (H₂O)₂] polymer is not well resolved, it is not interpreted but their μ_{eff} value shows that there are diamagnetic as expected.

The TGA data for the polymers are presented in Table-2. The weight loss of the polymer samples at different temperatures indicates that the degradation of the polymers is noticeable beyond 300°C. The rate of degradation becomes a maximum at a temperature lying between 400°C and 500°C depending upon the nature of the polymers. Each polymer lost about 56% of its weight when heated up to 700°C. Inspection of the thermograms of PTSA-Co(II), PTSA-Mn(II) and PTSA-Ni(II) samples revealed that these samples suffered appreciable weight loss in the range 150 to 280°C. This may be due to the presence of water strongly absorbed by the polymers. It has also been indicated earlier that the IR spectra of these three polymer samples have OH bands at around 3200 cm^{-1} due to associated water.

On the basis of the relative decomposition (% wt. loss) and the nature of thermograms, the polymers may be arranged in order in increasing stability as:



This trend also coincides with the stability order already reported for the metal oxinates [26] and for polymers of PTSA [24].

The antimicrobial activity of PTSA and its polymers are presented in Table-3 and 4. The data suggest that all the samples are toxic to bacteria or fungus. The data also suggest that the % age of bacteria or fungus is inhibited in the range of 58 to 81% depending upon the biospecies and polymers.

Ion-Exchange properties

The examination of data presented in Table-5 reveals that the amount of metal ions taken up by a given amount of the PTSA polymer depends upon the nature and concentration of the electrolyte present in the solution. The amounts of Fe(III) and Cu(II) ions taken up by the polymer sample increase with the increase in concentration of ions taken up by the polymer sample increase with the increase in concentration of ions like chloride, chlorate and nitrate but decrease with the increase in concentration of the sulfate ions. The amounts of the remaining three metal ions Co(II), Mn(II) and Zn(II) taken by the polymer sample decrease with the increase in concentration of chlorate, chloride, nitrate and sulfate ions.

Rate of metal uptake

The rates of metal absorption by the PTSA sample were measured for Fe(III), Cu(II) and Mn(II) ions presence of 1 M NaHCO₃ to know the time required to reach the stage of equilibrium. All experiments were carried out at pH 3. The examination of the results presented in Table.6 It shows that Fe(III) ions required slightly more than three hours for the establishment of equilibrium and Cu(II) and Mn(II) ions required about five hrs for the purpose. In the experiments with solution containing Fe(II) ions, more than 70% of equilibrium was established in the first hrs. This reveals that the rate of uptake of metal ions follows the order Fe(III) > Cu(II) > Mn(II). The rates of uptake of Zn(II) and Co(II) ions have been found to be very low at pH 3. Hence the values are no reported.

Distribution ratio of metal ions at different pH values

The results described in Table.7 reveal that the amount of metal ions taken up by the polymer sample PTSA at equilibrium increases with the increase in pH. The selectivity of the polymer sample Fe(III) ion is higher than that for each of the remaining metal ions. The distribution ratio for Fe(III) ions is lower than that for by about 1800 units at pH 3. The lower values of the distribution ratio for Fe(III) ions requires its attachment with proper sites on three different polymer chains and that of the ion requires such an attachment with sites on two polymer chains. Among the remaining metal ions, Cu(II) has a high value of distribution ration at pH 6 while the other three metal ions Co(II), Zn(II) and Mn(II) have a low distribution ration over a pH range from 4 to 6. Further work in the direction of wide range at such polymers and their ion exchanging properties are under progress.

Table. 5 Evaluation of the influence of different electrolytes in the uptake of several metal ions; ([Mt (NO₃)₂] = 0.1 mole · l⁻¹)^a

Metal ions	PH	[Electrolyte] (mole · l ⁻¹)	Adsorption of mmol. · 10 ¹ of the metal ion on PTSA polymer ^b .			
			NaClO ₄	NaNO ₃	NaCl	Na ₂ SO ₄
Cu ²⁺	5.5	0.01	0.18	0.15	0.19	0.34
		0.05	0.25	0.17	0.20	0.31
		0.1	0.24	0.22	0.21	0.30
		0.5	0.32	0.25	0.27	0.29
		1.0	0.53	0.27	0.33	0.25
Fe ³⁺	2.75	0.01	0.14	0.17	0.03	0.24
		0.05	0.30	0.23	0.07	0.11
		0.1	0.33	0.24	0.11	0.08
		1.0	0.44	0.30	0.30	0.06
Co ²⁺	5.5	0.01	0.24	0.22	0.16	0.12
		0.05	0.23	0.19	0.14	0.10
		0.1	0.15	0.18	0.13	0.08
		0.5	0.12	0.13	0.12	0.08
		1.0	0.08	0.09	0.08	0.06
Mn ²⁺	5.5	0.01	0.22	0.27	0.26	0.17
		0.05	0.20	0.26	0.24	0.16
		0.1	0.18	0.24	0.23	0.11
		0.5	0.16	0.23	0.22	0.07
		1.0	0.13	0.16	0.15	-----
Zn ²⁺	5.5	0.01	0.24	0.16	0.19	0.18
		0.05	0.23	0.17	0.17	0.16
		0.1	0.16	0.14	0.15	0.13
		0.5	0.14	0.11	0.08	0.08
		1.0	0.12	0.10	0.07	0.05

a. Volume of electrolyte solution 40 ml, time 24h, volume of metal ion solution 1ml, temp. 25 °C

b. Wt. of PTSA polymer 25 mg.

Table-6 Comparison of the rates of metal (Mt) ion uptake ^a

Time (h)	Attainment of equilibrium state ^b		
	Fe ³⁺	Cu ²⁺	Mn ²⁺
0.5	70.1	41.3	22.4
1	78.7	56.5	49.3
2	95.1	69.4	65.2
3	97.2	79.6	78.0
4	96.8	86.5	84.7
5	---	93.2	89.8
6	---	95.1	92.8
7	---	99.0	97.7

a. [Mt (NO₃)₂] = 0.1 mole.l⁻¹, volume 1 ml, [NaNO₃] = 1 mol.l⁻¹, volume 40 ml
pH = 3, temp 25° C, wt of PTSA polymer 25 mg.

b. Related to the amount of metal ions taken up at the state of equilibrium assumed to be established in 24 h and assumed to be 100%.

Table-7 Distribution ratios, D, of different metal ions as a function of the pH

pH	Distribution ratio of metal ions				
	Cu ²⁺	Co ²⁺	Mn ²⁺	Zn ²⁺	Fe ³⁺
1.5	----	----	----	----	----
1.75	----	----	----	----	175
2.0	----	---	----	----	200
2.5	----	---	----	----	480
3.0	165	----	170	----	1005
4.0	285	35	285	120	---
5.0	615	130	375	185	----
6.0	2870	390	440	320	---

CONCLUSION

The investigation described in the present article reveals the following conclusion:

Salicylic acid-formaldehyde polymer reacts with diazonium salt of p-toluidine and gives p-toluidine azo of Salicylic acid-formaldehyde (PTSA) polymeric ligand. The applicability of the polymeric ligand was explored by preparing polymeric chelates using different divalent metal ion indicating that the PTSA polymeric ligand has good chelating property and high thermal stability.

Further, the polymeric ligand is thermally more stable than its polymeric chelates. Among the five polymeric chelates, M-PTSA chelate is least stable, whereas M-PTSA polymeric chelates is the most stable having a thermal stability comparable to that of chelates may be used as heat resistant material up to 350°C. The polymeric ligand follows a two steps thermal degradation whereas polymeric chelates follow a single step thermal degradation.

A comparison of the thermal stability of the present polymeric chelates with those of Salicylic acid-formaldehyde with aniline as pendent groups of polymeric chelates reveals that the PTSA polymeric chelates are thermally more stable. Finally, the magnetic susceptibility results indicate that polymeric chelates of Cu(II), Ni(II), Fe(III), Mn(II) and Co(II) are paramagnetic, whereas that of Zn(II) is diamagnetic in nature.

All the polymers have good antibacterial as well as antifungal activity.

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