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Synthetic and Physico-Chemical Studies of Newly Synthesized Terpolymers Derived from Salicylaldehyde, Biuret and Trioxane#

S.V. BAWANKAR*, L.J. PALIWAL†, AND R.B. KHARAT‡
Department of Chemistry
J.B. College of Science, Wardha-440 001, India

Resins as copolymers which form a special class of polymers are widely known for their applications. SABT terpolymer resins were synthesized by the condensation of salicylaldehyde and biuret with trioxane in the presence of hydrochloric acid as catalyst and using varied molar ratios of the starting materials. Terpolymer resin compositions have been determined on the basis of their elemental analysis and the number average molecular weights of these terpolymer resins were determined by non-aqueous conductometric titration. The viscosity measurements carried out in DMF indicate normal behaviour. Spectral studies (IR, UV-visible and NMR) were carried out for structure elucidation and characterization of these terpolymers. TGA data were analysed to determine the characteristic and thermal stability of these resins. Electrical conductivity in solid state was ascertained to exhibit semiconducting character. Conclusively, ion exchange properties have been studied employing the batch equilibration method. In the light of all the physico-chemical and spectral evidences, the tentative structures have been proposed for SABT terpolymers.

INTRODUCTION

Research on high polymers or giant molecules (macromolecules) has been carried out principally due to its importance, currently attached to problems of producing materials with temperature lubricants, surface coatings, adhesive, fibres, elastomers, plastics, constructional materials for high speed aircrafts, space vehicles and ion exchangers. Various hydroxybenzoic acid-formaldehyde copolymers have been reported to find their use as ion exchangers[1, 2]. Patel and Joshi[3, 4] have prepared a resin from *o*/*p*-hydroxybenzoic acid, urea and formaldehyde in presence of acid catalyst. Manavalan and Patel[5, 6], have synthesized copolymers of salicylic acid-urea-formaldehyde. Terpolymers of salicylic acid-thiourea-trioxane and *p*-hydroxybenzoic acid-thiourea-trioxane have been syn-

Paper presented to National Symposium on Solid State Chemistry and Advanced Materials, Dec. 21–23, 1996. Department of Chemistry, University of Gorakhapur, Gorakhapur, India.
†Deptt. of Chemistry, Hislop College, Nagpur-440 0021, India.
‡Institute of Science, Nagpur-440 001, India.

thesized by various workers[7–10]. Pal and coworkers[11] prepared salicylic acid-biuret-trioxane terpolymers and their ion-exchange properties were studied. Terpolymers of salicylic acid-dithiobiuret-trioxane in presence of acid catalyst were also synthesized by Pal and found to be good semiconductors and ion exchangers[12]. However, no work has been carried out on the synthesis, characterization and ion-exchange properties of the terpolymer resins from salicylaldehyde, biuret and trioxane. The present work reports on the composition of these newly synthesized terpolymer resins and their characterization by the aforesaid various physico-chemical and spectral studies. The ion-exchange properties of these SABT terpolymer resins have been investigated. To corroborate the effectiveness of these resins as ion exchangers, the effects of pH, electrolyte concentration and time on ion exchange properties have been studied in detail.

EXPERIMENTAL

The chemicals used were all of AR or chemically pure grade, and wherever necessary purified further employing standard methods. DMF and DMSO were used after double distillation.

Synthesis of SABT Terpolymer Resins

The SABT terpolymer resins were prepared by condensing salicylaldehyde (SA) and biuret (B) with trioxane (T) in the mole ratio of 1 : 1 : 2/3, 1 : 2 : 1, 2 : 1 : 1, 3 : 1 : 4/3 and 4 : 1 : 5/3 respectively, in the presence of 2 M hydrochloric acid. The mixture were refluxed in the temperature range in an electrically heated oil bath for 5 h. The solid resinous product obtained was immediately removed from the flask after the reaction period was over. It was washed many times with cold water, dried and powdered. The powder was repeatedly washed with hot water to remove unreacted starting materials, if any. The air dried powder was extracted with ether to remove excess of salicylaldehyde-trioxane copolymer which might be present along with SABT terpolymer resin. It was further purified by dissolving in 2 N NaOH and filtered. It was then precipitated by dropwise addition of 1 : 1 (v/v) conc. hydrochloric acid/water with constant stirring in cold condition and filtered. The process was repeated twice. The resulting terpolymer resin was washed with hot water and dried in vacuum at room temperature. The purified terpolymer resins were finally ground well to pass through a 300 mesh size sieve and kept in vacuum over silica gel. The yields of these terpolymer resins were found to be 61–65% (Table-1) The purity of these terpolymer resins has been tested and confirmed by TLC.

The newly synthesized terpolymer resins along with m.p., yield and other reaction details are incorporated in Table-1.

Characterization of the Terpolymer Resins: The conductometric titration in nonaqueous medium, *i.e.*, DMF was applied for determination of number average molecular weights (Mn) using ethanolic KOH as a titrant. From the plots of specific conductance against milliequivalents of titrant base added, the first break and the last break were noted. The degrees of polymerization (DP) of the

terpolymer resin samples were obtained from the ratio of total milliequivalents of base used for neutralization of all the phenolic OH groups (last break) to the milliequivalents of base used for neutralization of first phenolic —OH group (first break). The DP thus obtained was multiplied by the weight[3–6, 11, 12] of the repeating unit to get number average molecular weight of the terpolymer sample.

$$Mn = \overline{Dp} \times \text{repeat unit weight}$$

Equip-Tronics digital conducitivity meter model No. EQ.DCM-P was used to measure the conductance of the solution.

The viscosities were determined using a Tuan-Fuoss[13] viscometer at six different concentrations ranging from 3 to 0.5% of terpolymer in DMF at 303 ± 0.1 K. Intrinsic viscosity (η) was calculated by Huggins equation (1) and Kraemer equation (2).

$$\eta_{sp/c} = [\eta] + K_1[\eta]^2 C \quad (1)$$

$$\text{In } \eta_{r/c} = [\eta] - K_2[\eta]^2 C \quad (2)$$

Electronic absorption spectra of the terpolymers in DMSO (spectroscopic grade) were recorded on Shimadzu double beam spectrophotometer in the range of 190–700 nm.

The IR spectra of all the five SABT terpolymers were scanned on Fourier transform infrared spectrophotometer in the wave number region of 4000–400 cm^{-1}

Proton NMR spectra were recorded on Varian-EM–360 A 60 MHz Proton NMR spectrometer. DMSO d^6 was used as a solvent.

TGA of SABT terpolymer resins was carried out by using Perkin-Elmer TGS-II Thermogravimetric Analyzer at heating rate of 15°C per minute in an inert atmosphere of nitrogen upto 820°C.

Semiconducting Propertes: The DC resistivity of all SABT terpolymers was ascertained in the temperature range 310 to 425 K by applying constant voltage of 50 volts across the pellets prepared from terpolymer resins. The measurements were made on BPL-Million-Megaohmmeter, model RM 160 MKIII. These measurements helped in the calculation of activation energy (E_a) of electrical conduction and deciding the semiconducting nature of the terpolymers.

Ion Exchange Properties: The ion-exchange properties of all the four SABT terpolymer resins have been determined by equilibration method[11, 14–18]. Experiments were carried out to study the influence of various electrolytes on the metal ion uptake, evaluation of the rates of metal ion uptake and distribution ratios of metal ions at different pH. The metal ions such as Co(II), Zn(II), Cd(II), Fe(III), Cu(II) and Ni(II) were considered for ion exchange studies.

RESULTS AND DISCUSSION

All the five SABT terpolymers are found to be light yellowish brown in colour having melting points in the range of 413–429 K (Table-1). These purified resins are found to be soluble in DMF, DMSO, aqueous NaOH and aqueous KOH.

Elemental Analysis: The SABT terpolymers were analysed for carbon,

hydrogen and nitrogen content (Table-2A). The elemental analysis data obtained are used to assign empirical formulae and the empirical formula weights to these terpolymer resins (Table-2A).

TABLE-1
SAMPLES AND REACTION DETAILS OF SABT TERPOLYMER RESINS

Reactants			Catalyst 2M HCl mL	Reflux Temp. ± 2 (K)	Terpolymer Abbreviation	Molar Ratio of reactants	Yield (%)	m.p. (K)
Salicyl aldehyde SA (Mole)	Biuret (Mole)	Trioxane (Mole)						
0.1	0.1	0.0600	100–150	403	SABT-1	1 : 1 : 2/3	61	413
0.1	0.2	0.1000	100–150	403	SABT-2	1 : 2 : 1	65	418
0.2	0.1	0.1000	100–150	403	SABT-3	2 : 1 : 1	65	423
0.3	0.1	0.1330	100–150	403	SABT-4	3 : 1 : 4/3	62	426
0.4	0.1	0.1666	100–150	403	SABT-5	4 : 1 : 5/3	63	429

TABLE-2
PERCENTAGE OF C, H AND N OF SALICYLALDEHYDE-BIURET-TRIOXANE TERPOLYMERS
(A)

Terpolymer	% Analysis, exp. (cclcd)			Empirical formula	Empirical formula weight	First stage of neutralization (meq /100 g of terpolymer)	Final stage of neutralization (meq per 100 g of terpoly mer)
	C	H	N				
SABT-1	52.8 (53.0)	4.6 (4.4)	16.4 (16.8)	$C_{11}H_{11}N_3O_5$	249	90	1100
SABT-2	47.8 (46.1)	4.5 (4,3)	22.2 (23.0)	$C_{14}H_{16}N_6O_6$	364	60	1040
SABT-3	58.3 (59.6)	4.6 (4.4)	11.4 (10.9)	$C_{19}H_{17}N_3O_6$	383	30	1100
SABT-4	59.9 (62.6)	4.7 (4.5)	8.4 (8.1)	$C_{17}H_{23}N_3O_8$	517	40	1100
SABT-5	66.1 (64.5)	4.65 (4.4)	6.5 (6.4)	$C_{35}H_{29}N_3O_{10}$	651	20	600

B

Terpolymer	Degree of Polymerization	Number Av. molecular wt. (Mn)	Intrinsic viscosity
SABT-1	12	3043	0.150
SABT-2	17	6309	0.190
SABT-3	36	14043	0.300
SABT-4	27	14217	0.385
SABT-5	30	19530	0.400

Molecular Weight: The number average molecular weight of SABT terpolymers has been determined by conductometric titration in DMF and the results are presented in Tables 2A and 2B, and titration curves are shown in Figs. 1 and 2.

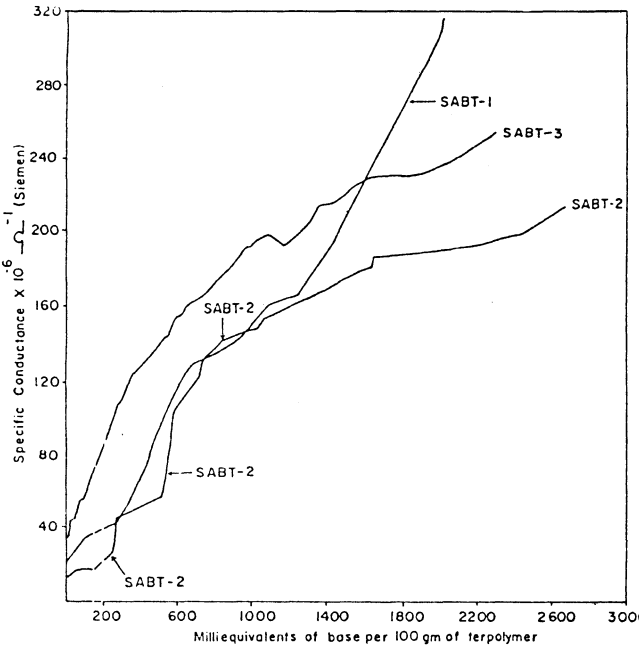


Fig. 1. Conductometric Titration Curves of SABT-1, SABT-2 and SABT-3 Terpolymers

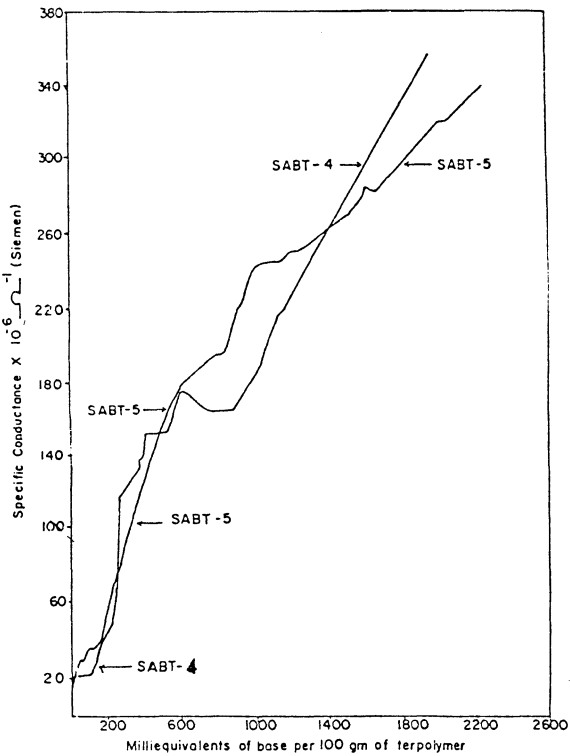


Fig. 2. Conductometric Titration Curves of SABT-4 and SABT-5 Terpolymers

The number average molecular weights of these terpolymers were found to be in the range of 3043–19530.

TABLE-3
VISCOSITY MEASUREMENT DATA FOR SABT TERPOLYMER
RESIN SOLVENT : N, N-DIMETHYL FORMAMIDE
Efflux Time for Pure Solvent (T_0) = 134.5 sec, Temperature 303 ± 0.1 K

Terpolymer	Polymer-concent ratio g dl^{-1}	Efflux time for Solution (t) in sec	Relative viscosity $\eta_{rel} = t/t_0$	Specific viscosity $\eta_{sp} = (t-t_0)t_0$	Reduced viscosity $\eta_{red} = \eta_{sp}/C$	ln η_{rel}	ln η_{rel}/C
SABT-1	0.5	144.3	1.073	0.072	0.146	0.070	0.140
	1.0	153.4	1.141	0.141	0.141	0.132	0.130
	1.5	160.7	1.195	0.194	0.129	0.178	0.110
	2.0	165.9	1.233	0.233	0.166	0.210	0.100
	2.5	168.4	1.252	0.252	0.100	0.225	0.090
	3.0	174.0	1.294	0.293	0.097	0.258	0.080
SABT-2	0.5	147.0	1.092	0.092	0.185	0.088	0.170
	1.0	157.8	1.173	0.173	0.173	0.160	0.160
	1.5	167.0	1.242	0.241	0.161	0.217	0.140
	2.0	176.0	1.309	0.308	0.154	0.270	0.130
	2.5	179.0	1.330	0.330	0.132	0.287	0.110
	3.0	180.0	1.214	0.338	0.113	0.291	0.090
SABT-3	0.5	163.0	1.294	0.211	0.432	0.194	0.380
	1.0	174.0	1.294	0.293	0.293	0.258	0.250
	1.5	195.0	1.449	0.449	0.299	0.371	0.247
	2.0	207.0	1.539	0.539	0.269	0.431	0.215
	2.5	222.0	1.650	0.650	0.260	0.501	0.200
	3.0	233.0	1.732	0.732	0.244	0.549	0.183
SABT-4	0.5	159.0	1.182	0.182	0.364	0.167	0.335
	1.0	185.0	1.377	0.377	0.375	0.320	0.320
	1.5	203.0	1.510	0.509	0.339	0.412	0.275
	2.0	222.0	1.655	0.650	0.325	0.504	0.252
	2.5	233.0	1.730	0.732	0.292	0.550	0.220
	3.0	235.0	1.740	0.747	0.249	0.558	0.186
SABT-5	0.5	162.0	1.206	0.204	0.408	0.187	0.375
	1.0	188.0	1.397	0.397	0.397	0.335	0.335
	1.5	213.0	1.583	0.583	0.389	0.459	0.306
	2.0	239.0	1.776	0.776	0.388	0.574	0.287
	2.5	255.0	1.895	0.895	0.358	0.639	0.255
	3.0	257.0	1.910	0.910	0.3035	0.647	0.215

Viscosity Measurements: The viscosity measurements data of SABT terpolymer resins were collected in Table 3 and the viscosity plots were given in Fig. 3. The intrinsic viscosity (η) was found to be 0.150, 0.190, 0.300, 0.385 and 0.400 dl/g for the terpolymers SABT-I, SABT-II, SABT-III, SABT-IV and SABT-V respectively at 303 K. It is observed that the value of intrinsic viscosity increases with the rising molecular weight of these terpolymer resins (Table-2B). It is consistent with the trend observed and explained by earlier research workers[5–6, 11, 12]

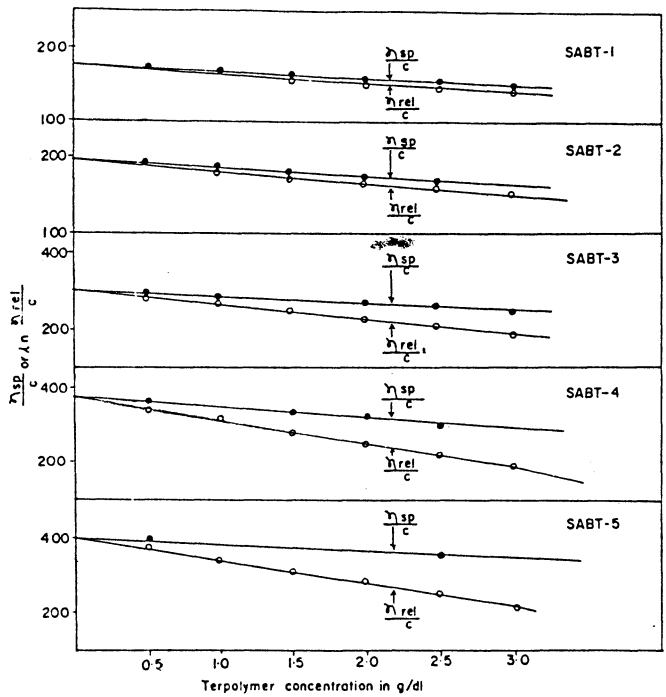


Fig. 3. Viscosity Plots of SABT Terpolymers

Electronic Spectral Studies: The electronic spectra of all SABT terpolymer resins are shown in Fig 4. All the terpolymers gave rise to two characteristic bands at 310–336 nm and 387–403 nm. These observed positions of the absorption bands indicate the presence of carbonyl group (aldehyde) possessing double bond which is in conjugation with the aromatic nucleus. The appearance of former band (more intense) can be accounted for $\pi \rightarrow \pi^*$ transition while the latter band (less intense) may be due to $n \rightarrow \pi^*$ electronic transition. The bathochromic shift from the basic value 280 nm and 328 nm respectively may be due to the effect of conjugation and presence of phenolic hydroxy group (auxochrome) at *ortho* position with respect to aldehyde group and highly substitued condition of benzene ring in the polymeric chain[19]. The appearance of phenolic hydroxy group as well affects the rise of ε_{max} value, *i.e.*, hyperchromic effect[19–24]. The ε_{max} value

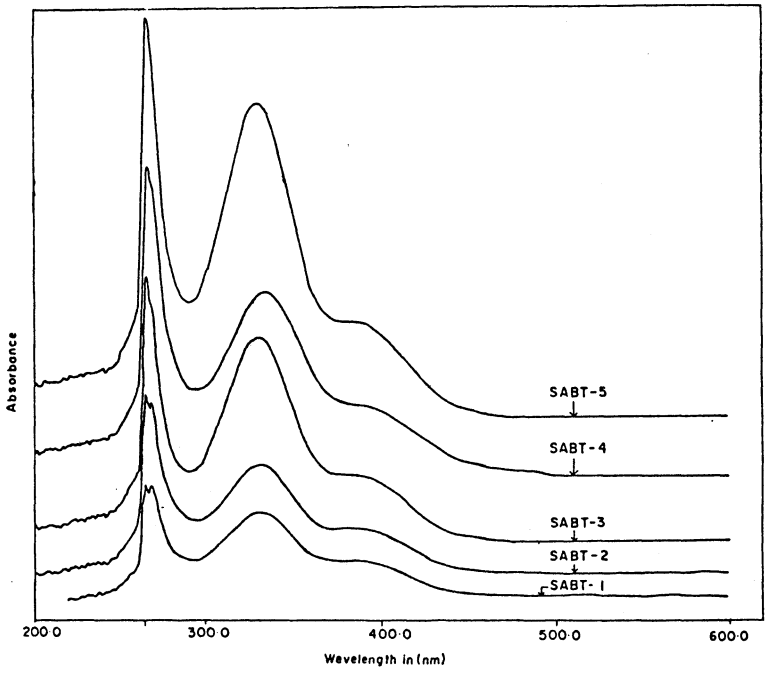


Fig. 4. Electron Absorption Spectra of SABT-1,2,3,4 and 5 Terpolymers

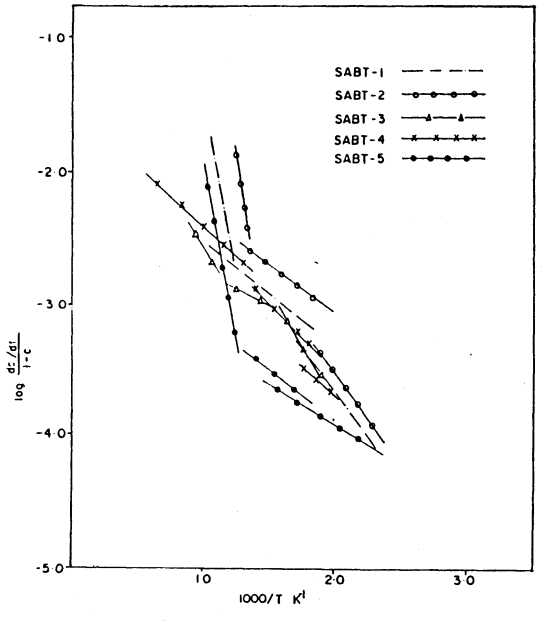


Fig. 5. Kinetic Plots of SABT-1,2,3,4 and 5 Terpolymers

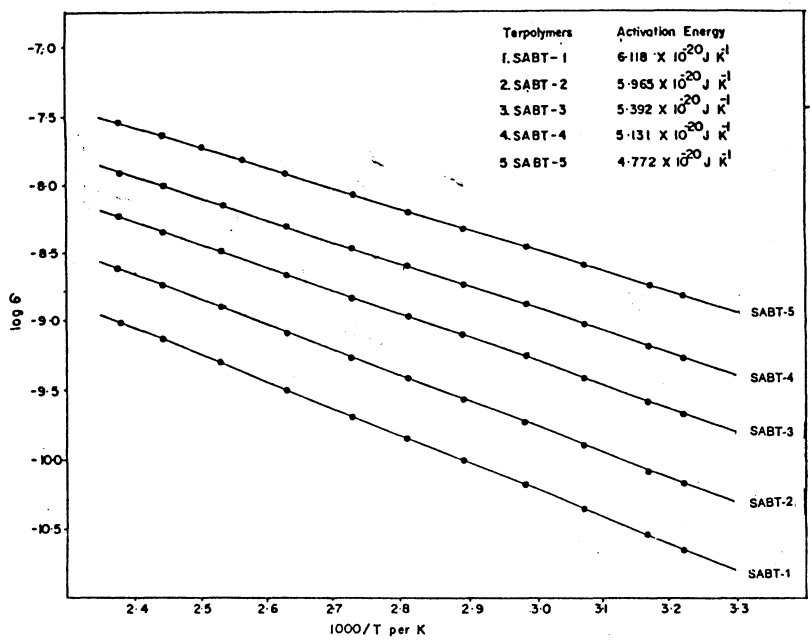


Fig. 6. Verification of Wilson's Expotential Law of Conductivity

gradually increases in the order: SABT-I < SABT-II < SABT-III < SABT-IV <SABT-V. This increasing order of ε_{max} values may be due to introduction of more and more chromophores (carbonyl group) and auxochromes (phenolic —OH group) in the repeated unit (monomer) of the terpolymer resins[19–25]. This observation is in good harmony with the proposed most probable structures of these terpolymers (Fig. 7.)

IR Spectral Studies: From IR spectral studies it has been revealed that all the SABT terpolymers give rise to nearly similar pattern of IR spectra. The IR spectral data are incorporated in Table-4. A broad and strong band appearing in the region 3500–3000 cm^{-1} may be assigned to the stretching vibration of phenolic (—OH) group. Very broad nature of the band clearly indicates the (—OH) group associated with intramolecular hydrogen bonding with carbonyl (aldehydic) group which is present at *ortho* position. Presence of (—NH—) group has been indicated by weak band at 3150–2925 cm^{-1} and sharp band at 800–760 cm^{-1} which suggests the stretching and bending vibrations respectively. The strong band displayed at 1670–1650 cm^{-1} may be due to the stretching vibration of (>C=O) group of both aldehydic as well as imide moiety. Two bands displayed at 2950–2850 cm^{-1} and 2850–2830 cm^{-1} are indicative of aldehydic (C—H) stretching vibration. Assignment of aromatic ring is made on the basis of strong and sharp band displayed at 1500 cm^{-1}. Besides, the aromatic (C—H) in-plane bending and out-of-plane bending are indicated by the bands at 1000 cm^{-1} and 850 cm^{-1}

respectively. A sharp and weak band obtained at 1150 cm^{-1} may be caused by 1,2,3,5-tetrasubstituted benzene ring. The methylenic (C—H) bending vibration is ascribed a sharp and weak band appearing at 1450 cm^{-1}. Sharp and medium band obtained at 1350 cm^{-1} can be interpreted in terms of (C—N) stretching vibrations Ar—CH_2—N< moiety[26-29].

TABLE 4
INFRA RED SPECTRAL DATA (cm^{-1}) OF SABT TERPOLYMER RESINS

Assignments	Observed band frequency (cm^{-1})					Expected band frequency (cm^{-1})	Ref
	SABT-1	SABT-2	SABT-3	SABT-4	SABT-5		
Phenolic (—OH) stretch	3500–3150	3500–3150	3500–3050	3050–3000	3500–2950	3500–3200	26, 29
(N—H) stretch (imide)	3150	3150	3050	3050	2925	3320–3140	19, 29
Aldehydic (C—H) stretch	2925	2950	2925	2925	2850	2900–2820	19, 29
	2850	2875	2850	2850	2730	2775–2700	
(>C=O) stretch (Aldehyde/Imide)	1650	1670	1650	1650	1650	1690–1650	19, 29
(N—H) bend (imide)	1550	1525	1550	1550	1550	1550–1510	19, 29
Aromatic ring vibration	1500	1500	1500	1500	1500	1600–1450	19, 29
Methylenic (C—H) bending vibration	1450	1450	1450	1440	1445	1485–1445	19, 29
(—C—N) stretch (Ar–CH_2—N— moiety)	1350	1390	1380	1390	1350	1350–1220	19, 29
Phenolic (C—O) stretching vibration	1270	1270	1270	1270	1290	1410–1310	19, 29
1,2,3,5, substitution of benzene ring	1150	1150	1150	1150	1150	above 800	19, 29
Aromatic (C—H) in-plane bending	1000	980	1000	1000	1050	1225–950	19, 29
Aromatic (C—H) out of-plane bending	820	820	850	850	850	900–860	19, 29
(N—H) bend (wagging imide)	780	780	760	760	800	800–666	19, 29

TABLE-5
NUCLEAR MAGNETIC RESONANCE SPECTRAL DATA OF SABT TERPOLYMERS

Chemical shift (δ') ppm of Terpolyers					Nature of proton assigned in PMR Spectra	Expected chemical shift	Ref.
SABT-1	SABT-2	SABT-3	SABT-4	SABT-5			
10.20	10.40	10.50	10.50	10.50	Aldehydicproton (Ar—CHO)	6.5–9.0	16, 26, 29
8.25	8.05	7.60	8.10	8.10	Phenolic proton (Ar—OH)	4.5–9.0	19, 20
7.20	7.25	7.06	7.25	7.15	Aromatic proton (Ar—H)	6.2–8.5	19, 29
6.75	5.60	4.90	–	6.75	Imido proton of —CO—NH—CO linkage	5.0–8.5	19, 20, 29
4.20	4.35	4.40	4.40	4.30	Amido proton of Ar—CH_2—NH—CO linkage	3.5–6.0	1920, 29
2.70	2.60	2.60	2.50	2.70	Methylenic proton of Ar—CH_2—N moiety	2.0–3.0	19, 20, 29

TABLE-6
RESULTS OF THERMOGRAVIMETRIC ANALYSIS OF SABT TERPOLYMER RESINS

Terpolymer Abbreviation	D_H (K)	% Weight loss at temperature T(K)							Onset Decomposition temp. (K)	First decomposition stage			Second Decomposition Stage		
		373	473	573	673	773	873	973		Temp range (K)	E	n	Temp range (K)	E	n
SABT-1	713	3.0	6.0	26	45	57	82	–	453	593–793	15.0	1	813–793	86.0	1
SABT-2	623	3.4	8.0	39	58	76	92	–	453	593–733	14.0	1	753–813	95.0	1
SABT-3	793	3.0	7.6	22	40	48	95	68	473	673–833	10.4	1	893–1113	28.0	1
SABT-4	753	2.0	5.5	16	41	52	59	78	593	753–913	12.7	1	933–1013	16.4	1
SABT-5	860	1.4	3.4	9	18	26	61	89	493	653–773	14.7	1	813–993	95.0	1

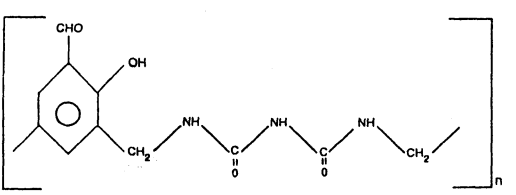
D_H = Half decompostion temperature in Kelvin E = Activation energy of thermal decomposition in kJ mol^{-1} n = Order of reaction

Nuclear Magnetic Resonance Spectra: The NMR spectra of SABT terpolymer resins show a signal at 10.4 ppm (δ) which may be due to aldehydic proton (Ar—CHO). The presence of phenolic proton is interpreted by the signal displayed in the region 7.6 to 8.25 δ. The multiple signals appeared at 7.05 to 7.25 ppm are the characteristics of aromatic protons which are not equivalent (highly substituted benzene ring)[20]. The signal which becomes intense in some cases at 4.9 to 6.7 ppm is indicative of imido protons of —CO—NH—CO—NH—CO linkage. A methylenic proton of Ar—CH_2—N— moiety is inferred by the appearance of a weak singlet signal at 2.5 to 2.7 ppm[19, 30, 31]. The spectral data are depicted in Table 5.

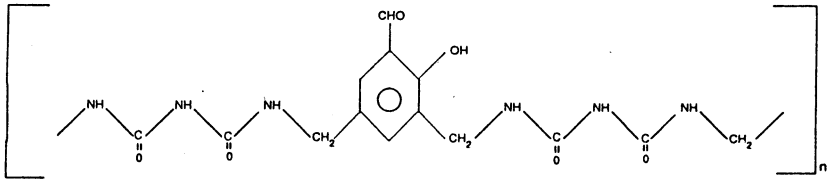
Thermogravimetric Analysis: The kinetic parameters of thermal degradation of terpolymer samples have been evaluated from thermograms using Sharp-Wentaworth's[32] method and the results of TG analysis of these resins are tabulated in Table 6. TG data of these SABT terpolymer resins revealed that the sample lost 2–5% of its weight when the temperature was raised to 453 K. This initial weight loss may be due to solvent or moisture entrapped in the terpolymer samples[5–6, 11–12]. All the SABT terpolymers have exhibited two decomposition stages for different terpolymer is found to be different. From the results of kinetic parameters it is concluded that the terpolymer resin synthesized from a higher molar ratio of salicyl aldehyde exhibited a lower rate of decomposition suggesting the order or stability as SABT-II < SABT-I < SABT-III < SABT-IV < SABT-V. This fact is further supported by the similar increasing order of melting points of these resins (Table 1). The above observed order of stability may be due to the possibility of an almost linear structure of the terpolymer having higher molar ratio of salicyl aldehyde which may give rise to a stable structure to the terpolymer chain[5, 6, 11, 12].

The results of TG analysis have suggested significant difference in activation energy (E_a) of different SABT terpolymer resins. These aromatic terpolymer resins have been found to exhibit a good magnitude of the thermal activation energy of decomposition process. The order of reaction at the first and second stages of decompostion was calculated to be unity. All the SABT terpolymers start decomposition after melting. From the results of the kinetic parameters it may be concluded that all these terpolymer resins follow approximately similar mechanism of degradation. However, it is difficult to draw any unique conclusion regarding the decomposition mechanism. It is worthwhile to be mentioned here that terpolymers SABT-I, SABT-II and SABT-V indicate 100% weight loss at experimental temperatures; however, the samples SABT-III and SABT-IV do not show complete decomposition even at high temperaturs which suggests the formation of some intermediate stable structures.

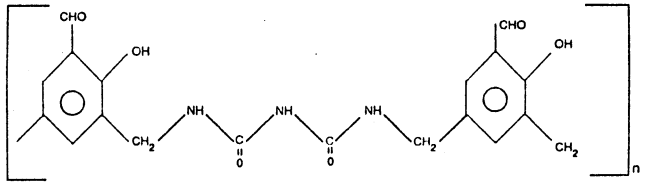
SABT- I



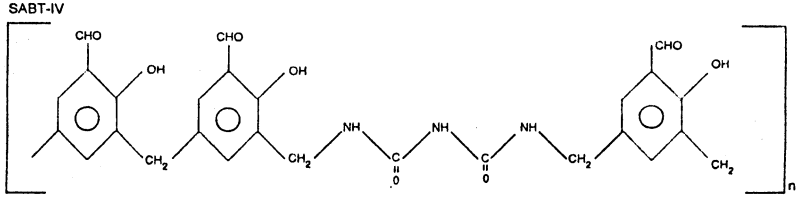
SABT- II



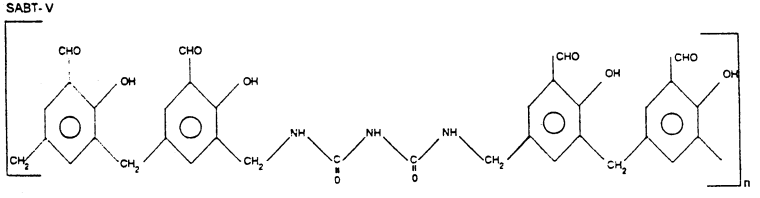
SABT- III



SABT-IV



SABT- V



On the basis of the all above physicochemical and spectral evidences the most probable tentative structure have been proposed for these new terpolymers which are given in Fig. 7

Electrical Conductivity: The temperature dependence of the electrical conductivity of these terpolymers is shown in Fig. 6. From the results of electrical conductiviy data, the following observations are made:

1. The electrical conductivity of SABT terpolymers at room temperature lies in the range of 2.3×10^{-11} to 3.1×10^{-8} ohm^{-1} cm^{-1}.
2. The plot of log σ versus 1/T is found to be linear in the temperature range under study, which indicates that the Wilson's exponential law $\sigma = \sigma_0 \exp^{(-Ea/KT)}$ is obeyed.
3. The energy of activation (E_a) of electrical conduction calculated from the slope of plots is found to be in the range of 4.77×10^{-20} to 6.11×10^{-20} JK^{-1}

4. The activation energy is found to decrease in the order SABT-I > SABT-II > SABT-III > SABT-IV > SABT-V and electrical conductivity is found to increase in the order SABT-I < SABT-II < 4-SABT-III < SABT-IV < SABT-V.
5. Electrical conductivity of each of these terpolymer resins increases with the increasing temperature; hence, these terpolymers may be ranked as semiconductors.

The electrical conduction of polymeric material depends upon incalculable parameters[33] such as porosity, pressure, method of preparation, atmosphere, etc. but activation energy (E_a) is not affected by these parameters and therefore it is fairly reproducible[34–36]. The magnitude of activation energy depends on the number of π electrons present in the semiconductor material. The more the number of π bonds, the lower the magnitude of activation energy (E_a) and vice-versa. Generally polymers containing aromatic nuclei in the backbone exhibit a lower activation energy than those with aliphatic system. Thus the low magnitude of activation energy may be due to the presence of large number of π electrons in the polymer chain. Moreover, the increasing order of electrical conductivity and decreasing order of activation energy of electrical conduction as shown above may be due to introduction of more aromatic skeleton (and therefore more and more π electrons) in the repeat unit structure of terpolymers, which is in good agreement with the most probable structures proposed for the newly synthesized SABT terpolymer resin. Thus, it can be concluded that these types of terpolymers may be used as semiconducting materials in various industries.

Application of SABT terpolymer Resins as Ion Exchangers

All the experiments were conducted in duplicate and the results were found to be reproducible. The results of the batch equilibrium study carried out with the terpolymer resin sample SABT-I, SABT-II, SABT-III, SABT-IV and SABT-V. are presented in Tables 7–9. From the study carried out with eight six ions under experimental conditions, certain generalizations may be made about the behaviour of SABT terpolymer resin samples.

Influence of Electolytes on the Metal Ion Uptake: The data presented in Table-7 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 Cu(II), Fe(III) and Ni(II) ions taken up by the terpolymer resins increases with the increase in concentration of the electrolyte, whereas in presence of sulphate ions the amount of the above mentioned ions taken up by the terpolymer samples decreases with increasing concentration of the electrolyte[3, 11, 12, 16, 17, 33]. Moreover, the amount of Cd(II), Co(II), Zn(II) ions taken up by the terpolymer samples increases with increasing concentration of the chloride, nitrate, perchlorate and sulphate ions[3, 11, 12, 16, 17, 33]. This trend can be interpreted in terms of the effect of these electrolytes on the stability constant of the said metal ions with terpolymers.[34] This type of trend has also been observed by other investigators in related fields.[3, 11, 12, 16, 17, 33]

TABLE-7
EVALUATION OF INFLUENCE OF DIFFERENT ELECTROLYTES ON THE UPTAKE OF METAL FOR SABT TERPOLYMER

Metal	Concentration	Na_2SO_4					NaCl					$NaNO_3$					$NaClO_4$				
		SABT-1	SABT-2	SABT-3	SABT-4	SABT-5	SABT-1	SABT-2	SABT-3	SABT-4	SABT-5	SABT-1	SABT-2	SABT-3	SABT-4	SABT-5	SABT-1	SABT-2	SABT-3	SABT-4	SABT-5
Co(II)	0.01	2.06	2.06	2.28	2.35	2.43	1.76	1.84	1.98	1.98	2.13	1.76	1.98	2.28	2.43	2.57	1.76	1.76	1.91	1.98	2.13
	0.05	1.62	1.76	1.91	2.20	2.35	1.03	1.39	1.39	1.54	1.62	1.39	1.61	1.69	1.69	1.84	1.47	1.62	1.76	1.76	1.91
	0.10	1.17	1.47	1.62	1.84	1.98	0.81	1.10	1.10	1.25	1.39	1.25	1.54	1.62	1.69	1.84	1.03	1.17	1.32	1.47	1.62
	0.50	0.88	0.88	1.03	1.32	1.47	0.66	0.73	0.73	0.88	1.03	0.89	1.25	1.25	1.39	1.54	0.73	0.81	1.25	1.47	1.47
	1.00	0.58	0.58	0.58	0.88	1.03	0.29	0.29	0.51	0.66	0.81	0.88	0.36	0.36	0.81	0.95	0.44	0.51	0.51	0.66	0.73
Zn(II)	0.01	1.55	1.71	1.96	2.12	2.28	2.86	2.91	3.02	3.10	3.26	2.12	2.45	2.69	2.77	2.86	2.53	2.77	3.02	3.10	3.18
	0.05	1.22	1.38	1.63	1.63	1.79	2.53	1.06	1.06	1.38	1.47	2.04	2.04	2.12	2.20	2.36	2.20	2.61	2.77	3.02	3.10
	0.10	0.98	1.22	1.22	1.38	1.55	0.81	0.89	1.06	1.22	1.30	0.57	0.65	0.98	1.63	1.79	1.63	1.79	1.96	2.86	3.02
	0.50	0.72	0.65	0.73	1.30	1.47	0.49	0.57	0.73	0.89	0.98	0.40	0.49	0.73	1.06	1.22	0.89	1.22	1.55	1.38	1.55
	1.00	0.40	0.40	0.40	0.89	1.06	0.32	0.32	0.49	0.65	0.73	0.32	0.40	0.65	0.73	0.89	0.73	0.89	0.81	0.89	0.98
Cd(II)	0.01	1.40	1.68	2.24	2.24	2.52	2.10	2.10	3.38	2.38	2.66	2.24	2.38	2.38	2.52	2.66	1.68	1.96	2.10	2.10	2.38
	0.05	1.26	1.68	1.82	1.96	2.24	1.54	1.68	1.96	2.10	2.38	1.82	2.24	2.24	2.38	2.52	1.40	1.54	1.68	1.82	2.10
	0.10	1.12	1.54	1.54	1.80	2.10	1.26	1.40	1.68	1.68	1.82	1.82	1.82	1.96	2.10	2.24	1.26	1.26	1.40	1.54	1.82
	0.50	0.70	0.84	0.98	1.26	1.54	0.98	0.98	0.98	0.84	1.12	1.26	1.68	1.26	1.40	1.54	0.70	0.28	0.84	0.84	1.12
	1.00	0.15	0.70	0.70	0.84	1.12	0.07	0.12	0.56	0.70	0.98	0.98	1.26	0.84	0.98	1.12	0.56	0.56	0.70	0.70	0.98

Metal	Concentration	Na_2SO_4					NaCl					$NaNO_3$					$NaClO_4$				
		SABT-1	SABT-2	SABT-3	SABT-4	SABT-5	SABT-1	SABT-2	SABT-3	SABT-4	SABT-5	SABT-1	SABT-2	SABT-3	SABT-4	SABT-5	SABT-1	SABT-2	SABT-3	SABT-4	SABT-5
Fe(III)	0.01	2.51	2.58	2.72	2.79	2.93	0.62	0.76	0.76	0.83	0.97	1.32	1.25	1.39	1.46	1.53	1.04	1.10	1.18	1.30	1.50
	0.05	1.53	1.60	1.67	1.74	1.88	1.11	1.18	1.20	1.11	1.46	1.74	1.81	1.88	1.95	2.02	2.02	2.09	2.30	2.50	2.60
	0.10	1.39	1.53	1.60	1.67	1.74	1.95	1.39	1.67	2.16	2.30	2.09	2.16	2.23	2.30	2.37	2.30	2.51	2.50	2.60	2.70
	0.50	0.97	0.97	1.04	1.04	1.18	2.30	2.79	2.16	2.58	2.72	2.30	2.44	2.51	2.65	2.72	2.60	2.72	2.50	2.90	2.80
	1.00	0.34	0.34	0.41	1.04	1.18	3.42	3.42	2.86	3.35	3.49	2.65	2.86	2.93	3.07	3.14	3.07	2.93	3.00	3.20	3.40
Co(II)	0.01	3.57	3.81	4.60	4.68	4.84	1.50	2.38	2.93	3.09	3.25	2.62	2.85	2.01	3.17	3.41	2.22	2.65	2.93	3.01	3.17
	0.05	2.66	3.41	3.73	3.88	3.97	2.46	3.17	3.65	3.81	3.97	3.33	3.73	2.73	3.89	4.05	2.62	3.57	3.49	3.97	1.13
	0.10	2.06	2.06	2.22	2.38	2.38	2.93	3.41	4.13	4.28	4.28	3.25	3.89	4.02	4.13	5.52	3.08	4.13	4.68	5.16	5.24
	0.50	1.19	1.35	1.35	1.58	1.74	3.57	3.97	4.36	4.07	4.76	3.41	4.13	4.44	4.60	4.76	3.57	4.36	5.08	5.48	5.56
	1.00	0.39	0.39	0.39	0.63	0.79	3.81	4.44	5.56	5.63	5.79	3.65	5.40	4.63	5.71	5.87	4.92	5.32	5.40	5.79	5.87
Ni(II)	0.01	2.71	3.08	3.44	3.66	3.81	0.88	1.02	1.46	1.68	1.83	0.73	0.80	1.02	1.17	1.32	1.17	1.24	1.39	1.54	1.68
	0.05	1.39	1.68	2.71	3.44	3.59	1.17	1.24	1.98	2.05	2.20	0.80	1.02	1.17	1.24	1.39	1.20	1.68	1.68	2.05	2.20
	0.10	1.24	1.61	1.83	2.71	2.86	1.46	1.76	1.17	2.42	2.56	1.61	1.24	2.27	1.34	2.49	1.40	2.05	2.05	2.12	2.27
	0.50	1.02	1.39	1.61	2.56	2.71	1.68	1.98	2.05	2.49	2.64	1.76	2.27	2.64	3.18	3.22	1.54	2.05	2.27	2.71	2.78
	1.00	0.44	0.58	0.80	0.88	1.02	3.00	3.08	3.22	3.22	3.44	2.49	2.56	3.74	5.28	5.42	1.98	2.34	2.71	3.08	3.22

It was also found that the amount of metal ions taken up by SABT terpolymer resins increases in the order SABT-I < SABT-II < SABT-III < SABT-IV < SABT-V. This observed order of terpolymers is due to incorporation of more number of donor groups in the repeat unit of terpolymer resin samples.

TABLE-8
COMPARISON OF THE RATES OF METAL ION UPTAKE AT 300 K

Metal Ion	Terpolymer	Percentage of the amount of Metal ion taken up at different times (h)						
		0.5	1.0	2.0	3.0	4.0	5.0	6.0
Cd(II)	SABT-1	11.0	24.2	42.3	56.2	71.1	82.2	94.0
	SABT-2	14.0	28.3	45.4	61.8	75.7	86.1	94.2
	SABT-3	17.0	29.7	44.1	59.5	81.9	89.2	95.0
	SABT-4	19.0	31.4	48.7	64.3	88.2	92.1	95.7
	SABT-5	21.0	33.7	50.5	67.5	95.5	93.5	97.1
Co(II)	SABT-1	10.1	17.4	28.3	44.0	58.4	70.6	91.1
	SABT-2	11.3	20.4	30.6	44.3	61.5	73.5	92.9
	SABT-3	14.8	23.5	33.1	46.8	63.6	77.8	95.0
	SABT-4	21.2	27.5	39.0	49.5	70.6	80.6	95.3
	SABT-5	27.8	31.6	45.1	52.5	77.2	83.5	96.2
Cu(II)	SABT-1	27.8	31.9	36.7	46.9	56.6	78.2	91.3
	SABT-2	30.5	35.9	53.7	64.5	75.6	84.6	91.8
	SABT-3	33.1	39.4	46.0	58.7	76.5	84.2	94.9
	SABT-4	35.6	40.5	50.4	68.8	80.7	87.1	96.3
	SABT-5	38.1	41.6	54.9	78.9	84.9	90.0	97.7
Fe(III)	SABT-1	37.6	40.2	48.9	55.9	81.5	95.8	–
	SABT-2	39.2	44.8	54.0	63.0	83.4	97.0	–
	SABT-3	41.2	47.4	57.0	64.8	86.5	97.4	–
	SABT-4	44.7	52.3	66.8	73.0	89.5	97.8	–
	SABT-5	48.7	55.9	70.4	76.0	93.1	101.4	–
Ni(II)	SABT-1	13.8	22.7	30.9	39.2	55.6	68.4	91.5
	SABT-2	17.4	23.6	34.9	48.7	71.2	68.5	93.0
	SABT-3	19.6	30.2	43.0	56.4	79.8	81.2	95.3
	SABT-4	22.2	32.0	57.1	71.3	80.8	92.2	97.8
	SABT-5	24.8	33.8	71.2	86.2	81.9	103.3	100.3
Zn(II)	SABT-1	11.0	20.4	36.6	50.1	60.9	69.0	90.2
	SABT-2	13.3	24.5	37.4	52.0	66.1	74.1	95.5
	SABT-3	16.4	29.7	42.9	55.9	69.3	77.1	95.0
	SABT-4	16.9	34.3	46.8	59.7	72.8	80.9	95.5
	SABT-5	17.5	38.5	50.7	63.5	75.8	84.1	95.8

Effect of Time on the Rate of Metal Uptake: The rates of metal ion absorption by all the five SABT terpolymer resins were measured for Cd(II), Co(II), Cu(II),

Fe(II), Ni(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 resin samples.

TABLE-9
DISTRIBUTION RATIO (D) OF DIFFERENT METAL IONS
AS FUNCTION OF pH AT 300 K

Metal Ion	Terpolymer	Distribution ratio of metal ions at various pH								
		1.5	1.75	2.0	2.5	3.0	4.0	5.0	6.0	6.5
Cd(II)	SABT-1	–	–	–	–	13.6	29.8	35.8	72.0	125.2
	SABT-2	–	–	–	–	15.7	32.2	44.5	77.3	140.7
	SABT-3	–	–	–	–	18.6	35.4	45.7	78.7	158.6
	SABT-4	–	–	–	–	20.7	38.9	48.7	80.9	167.1
	SABT-5	–	–	–	–	22.9	32.2	51.6	83.4	176.5
Co(II)	SABT-1	–	–	–	17.4	24.7	35.3	103.8	152.7	163.2
	SABT-2	–	–	–	19.3	27.3	62.5	106.0	161.1	165.5
	SABT-3	–	–	–	23.2	31.6	66.5	109.4	163.7	169.7
	SABT-4	–	–	–	26.3	32.7	71.8	110.9	187.0	210.4
	SABT-5	–	–	–	29.8	33.3	76.8	112.3	206.5	240.1
Cu(II)	SABT-1	–	–	–	28.7	31.6	200.7	1039.0	650.8	1174.5
	SABT-2	–	–	–	35.2	38.5	222.8	1067.5	665.3	1187.5
	SABT-3	–	–	–	39.1	52.1	239.4	1130.8	686.1	1215.5
	SABT-4	–	–	–	44.0	65.5	242.8	1158.1	712.7	1263.2
	SABT-5	–	–	–	51.0	70.0	249.3	1188.1	740.2	1310.0
Fe(III)	SABT-1	11.7	132.2	248.2	390.5	–	–	–	–	–
	SABT-2	12.8	163.8	275.5	486.5	–	–	–	–	–
	SABT-3	14.1	157.9	277.5	480.5	–	–	–	–	–
	SABT-4	16.7	165.1	283.9	499.1	–	–	–	–	–
	SABT-5	19.4	174.3	194.1	505.8	–	–	–	–	–
Ni(II)	SABT-1	–	–	–	17.8	27.6	109.6	234.8	248.4	250.1
	SABT-2	–	–	–	19.2	32.1	137.0	285.7	257.8	251.6
	SABT-3	–	–	–	23.0	46.0	152.58	327.9	277.7	258.9
	SABT-4	–	–	–	34.9	52.9	202.8	353.5	453.7	895.9
	SABT-5	–	–	–	46.8	59.8	250.4	378.2	503.5	936.8
Zn(II)	SABT-1	–	–	–	17.2	37.1	72.4	75.3	133.5	217.7
	SABT-2	–	–	–	18.7	38.6	80.9	82.2	153.1	228.7
	SABT-3	–	–	–	20.0	43.4	94.9	117.2	164.8	237.7
	SABT-4	–	–	–	21.9	47.2	96.7	122.8	168.8	240.1
	SABT-5	–	–	–	23.5	51.5	98.9	128.1	173.5	242.6

Metal ion concentration = 0.1 mole/L; vol. = 2 mL;
$NaNO_3$ concentration = 1.0 mole/L; vol. = 25 mL;
Related to the amount of metal ion in the state of equilibrium (100%).

The experimental results (Table-8) indicate that the time taken for the uptake of the different metal ions at a given stage depends on the nature of the metal ion under given conditions. The rate of metal ion uptake follows the order : Fe(III) > Cu(II) > Ni(II) > Co(II) > Zn(II) > Cd(II). Futhermore, it is revealed that the rate of metal uptake follows the order SABT-I < SABT-II < SABT-III < SABT-IV < SABT-V.

Distribution Ratio of Metal Ions as a Function of pH: The experimental results of the effect of pH on the amount of metal ions distributed between two phases are tabulated in Table-9. It is seen from Table 9 that the relative amount of metal ions taken up by the terpolymer resins increases with rising pH of the medium. The magnitude of increase, however, is different for different metal ions.[11, 12, 36] The interesting observation is that the SABT shows selectivity towards Fe(III) over other metal ions under study. The selectivity of metal cations by the SABT terpolymers showed the following trend by Fe(III) > Cu(II) > Ni(II) > Co(II) > Zn(II) > Cd(II). Thus such type of studies are helpful for the selective uptake of a particular metal ion from a mixture of different metal ions at particular pH[11, 12, 36]. It can be concluded that these resins can be used for the separation of Fe(III) from the metal ions effectively.

$$D = \frac{\text{Weight (in mg) of metal ion taken up by 1 g of terpolymer}}{\text{Weight (in mg) of metal ion taken up by 1 mL of solution}}$$

Metal ion concentration = 0.1 mole/litre; Volume = 2 mL;
Concentration of $NaNO_3$ = 1.0 mole/litre; Volume = 25 mL;
Time = 24 h (equilibrium state); Error 3.0%, Temperature = 300 K

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