Polymer–metal complexes of amino functionalized divinylbenzene-crosslinked polyacrylamides

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The complexation of amino functions supported on polyacrylamides with 2–20 mol% of divinylbenzene (DVB) crosslinks was investigated towards Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) ions. With increasing extent of DVB-crosslinking, the metal ion intake decreased in the order: Hg(II) ≫ Cu(II) > Zn(II) > Ni(II) > Co(II). The polymeric ligand and the derived metal complexes were characterized by their typical i.r. absorptions and from the e.s.r. spectra. The i.r. absorptions of the polymeric ligands were shifted by complexation. The e.s.r. parameters suggested the distorted tetragonal geometry of the Cu(II) complexes. The change in surface morphology on complexation was followed by scanning electron microscopy. The thermal stability varied with the incorporation of metal ions. The activation energy values and the extent of crosslinking in Cu(II) complexes fit into the general equation for a cubic polynomial. The time-course and kinetics of complexation and the adsorption characteristics of complexation were also followed. The swelling characteristics varied with the extent of crosslinking, and the extent of swelling was lower for the complexed resins. The complexed resins can be recycled several times, and the Cu(II)-desorbed resin showed specificity to the Cu(II) ion in the presence of other metal ions.

(Keywords: crosslinked polyacrylamide; polymer–metal complexes; thermogravimetry; specificity)

INTRODUCTION

The study of the complexation behaviour of polymer-supported ligands with metal ions is of significance in various branches of chemistry[1–3]. The complexation of a polymer-supported ligand is governed by a number of factors characteristic of the macromolecular matrix. The ligand function is a relatively small part of the polymer matrix. Its complexation behaviour is decided by the microenvironment around the ligand functions such as the nature of the polymer backbone[4], the nature and extent of crosslinking[5], and separation of the ligand function from the three-dimensional macromolecular matrix[6]. Study of the interdependence of these factors with the reactivity of attached functional groups forms the basis of a number of types of functional and speciality polymers[7–9]. This paper describes in detail the complexation behaviour of amino functions supported on polyacrylamides with 2–20 mol% of DVB-crosslinks towards Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) ions, their characterization by i.r., e.s.r., t.g. and SEM analysis, complexation kinetics, recyclability, specificity and swelling characteristics.

EXPERIMENTAL

General

All the reagents were of certified ACS reagent grade. The purest available metal salts were used to prepare metal ion solutions. The i.r. spectra were recorded on a Perkin Elmer 983 i.r. spectrophotometer, and e.s.r. spectrum on a Varian E-12 instrument at room temperature. Thermogravimetric curves were recorded on a Delta Series TGA-7 Thermal Analyser at a heating rate of 20°C min^{-1} under nitrogen atmosphere.

Synthesis of DVB-crosslinked polyacrylamides

DVB-crosslinked polyacrylamides were prepared by free radical solution polymerization. For the preparation of 2% DVB-crosslinked polymer, acrylamide (20.9 g) and divinylbenzene (1.3 g) were dissolved in ethanol (100 ml). Benzoylperoxide (200 mg) was added, and the mixture was heated with stirring at 70°C for 4 h. The polymer formed was collected by filtration, washed several times with water, ethanol, benzene and methanol, and dried at 70°C. Polyacrylamides with 4, 8, 12 and 20 mol% of DVB-crosslinks were prepared by varying the mol% of the monomers.

Transamidation of DVB-crosslinked polyacrylamides: Preparation of poly(N-2-aminoethylacrylamide)s

Ethylenediamine (100 ml) was added to polyacrylamide (10 g) by stirring. The mixture was heated at 100°C for 9 h. The reaction mixture was poured into water (1 l) containing crushed ice. The resin was filtered and washed with NaCl solution (0.1 M) until the filtrate was free from ethylenediamine, as indicated by the absence of any blue coloration with ninhydrin reagent. The gel was washed with water (to remove NaCl) and with methanol, and dried at 70°C.

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Estimation of resin amine content

Amino resin (100 mg) was equilibrated with HCl (0.2 N, 10 ml) with stirring for 24 h. The resin samples were filtered, washed with distilled water to remove unreacted HCl, and the filtrate was titrated against NaOH (0.2 N) to a phenolphthalein end point.

Complexation of metal ions with amino resins

The complexation of amino resins with varying extents of DVB crosslinks was carried out with Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) ions using the batch equilibration method. First, 200 mg each of the resin samples was stirred with a definite concentration of excess metal salt solution at its natural pH (0.03 N, 50 ml) for 24 h. The complexed resins were collected by filtration, and washed with distilled water to remove uncomplexed metal ions. The concentrations of metal salt solutions were estimated by volumetric methods: Cu(II) by iodometry, Ni(II) by direct EDTA titration using mureoxide indicator, and Zn(II), Co(II) and Hg(II) by direct EDTA titration using xylenol orange as the indicator[10].

Time-course of complexation

Batch studies were carried out with 500 mg of 4% DVB-crosslinked amino resin to optimize the duration for maximum complexation. Co(II), Ni(II), Cu(II) and Zn(II) solutions (100 ml each) were added to the amino resins and stirred. Aliquots (2 ml each) were withdrawn from the test solutions at regular intervals and estimated.

Kinetics of complexation

Different sets of 8% DVB-crosslinked amino resin (100 mg) were stirred with Cu(II) salt solution (6×10^{-3} M, 100 ml) at room temperature (306 K) and 318 K in a thermostatically controlled system for varying time intervals. The remaining concentration of Cu(II) ions in each case was estimated.

Adsorption studies

Different sets of 100 mg of 8% DVB-crosslinked amino resin were equilibrated with Cu(II) salt solution of varying concentrations at two different temperatures (303 K and 316 K). The temperatures of the complexation/adsorption was maintained constant using a thermostat. The Langmuir and Frumkin equations were used for the adsorption studies.

Recyclability of complexed resin

A sample (500 mg) of the Cu(II) complex with 4% crosslinking was stirred with 2 N sulfuric acid (15 ml) for 2 h. The desorbed Cu(II) ions were collected by filtration, and estimated after neutralization. The resin left after the acid-treatment was washed with dilute sodium hydroxide and distilled water, and again subjected to complexation.

Swelling studies

The amino resins (500 mg each) were equilibrated with 30 ml of distilled water for four days. The swollen resins were collected by filtration, adhering traces of water were removed by pressing with filter paper and the samples were weighed. The swollen resins were dried in a vacuum for 24 h and weighed again. Another set of amino resins was equilibrated with 30 ml Cu(II) salt solution containing 55 mg Cu(II) ions, and the weights of the wet and dried resins were followed. From the swollen and dry weights of the samples the equilibrium water content (*EWC*) was calculated using the equation:

$$EWC = \frac{\text{Wt. of wet resin} - \text{Wt. of dry resin}}{\text{Wt. of wet resin}} \times 100$$

RESULTS AND DISCUSSION

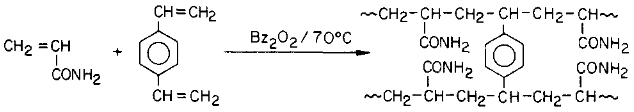
Preparation of DVB-crosslinked polyacrylamides

Polyacrylamides with varying extents (2–20 mol%) of DVB crosslinks were prepared by solution polymerization of the monomers in ethanol at 70°C, with benzoylperoxide as the initiator as represented in *Scheme 1*. A commercial sample which contains 55% of divinylbenzene was used for the polymerization. The mol% of the crosslinking agent for the preparation of DVB-crosslinked polyacrylamides were taken on this basis. The composition of the feed for the preparation of crosslinked polymers varied from 2 to 20 mol% of divinylbenzene (*Table 1*).

The introduction of hydrophobic DVB crosslinks imparts rigidity and hydrophobicity to the crosslinked polymers, and it increases with an increasing number of DVB crosslinks. These resins are powdery in nature, and they swell less in water than the NNMBA- and TEGDA-crosslinked resins[11]. The introduction of DVB crosslinks imparts increased swelling of the resin in organic solvents to those with hydrophilic crosslinking agents[12]. This would favour reactions in organic media.

Transamidation of DVB-crosslinked polyacrylamides: Preparation of aminopolyacrylamides

Transamidation reactions of polyacrylamides with low molecular weight amines were used for the preparation of amino functional polymers[13]. In the transamidation of DVB-crosslinked polyacrylamides, ethylenediamine itself was used as the solvent and the reaction was carried out at 100°C (*Scheme 2*). In transamidation using diamines, the possibility of transamidation of both the amino functions of same diamine leads to additional crosslinking, which lowers the swelling of the resins; the extent of this is the same in all resins.



Scheme 1 Preparation of DVB-crosslinked polyacrylamides

$$\sim CONH_2 + H_2NCH_2CH_2NH_2 \xrightarrow[9h]{100°C} \sim CONHCH_2CH_2NH_2$$

Scheme 2 Transamidation of DVB-crosslinked polyacrylamides with ethylenediamine

Table 1 Preparation of DVB-crosslinked polyacrylamides

DVB (mol%)	Acrylamide (g)	DVB (g)	Yield (g)
2	20.87	1.30	18.00
4	20.50	3.15	17.54
8	19.60	6.30	17.55
12	18.70	9.45	15.65
20	17.00	15.75	21.37

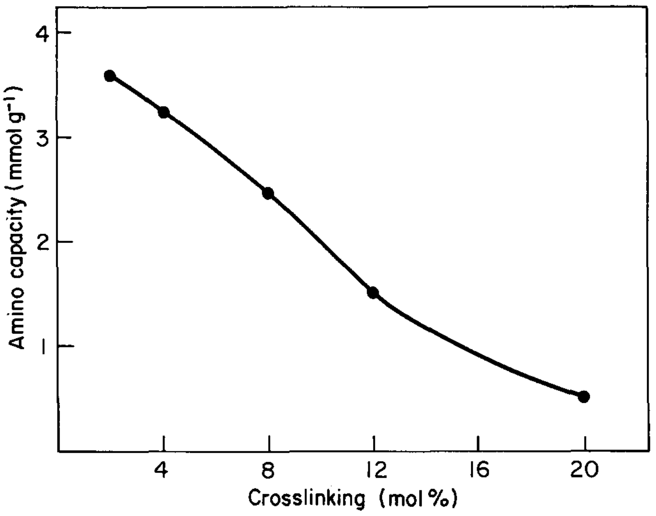


Figure 1 Amino capacity *versus* extent of DVB crosslinking

Table 2 Metal ion intake by DVB-crosslinked amino resins

DVB (mol%)	Metal intake in mg g^{-1} (meq g^{-1}) Co(II)	Ni(II)	Cu(II)	Zn(II)	Hg(II)
2	47 (0.80)	38 (0.61)	173 (2.41)	130 (1.41)	797 (3.97)
4	43 (0.73)	36 (0.61)	153 (2.41)	92 (1.41)	704 (3.51)
8	19 (0.32)	21 (0.36)	83 (1.31)	57 (0.87)	402 (2.00)
12	5 (0.08)	15 (0.26)	65 (1.02)	22 (0.34)	308 (1.54)
20	– (–)	– (–)	12 (0.20)	– (–)	116 (0.58)

The amino functions were detected using the semi-quantitative ninhydrin reaction[14]. The yields and the amino capacities of the aminoethyl derivatives vary with the extent of DVB content. The yields of the low crosslinked systems are less because of the operational losses arising from the decreased mechanical stability. With increasing DVB content, the rigidity of the polymer increases, and the yields are higher for the high crosslinked systems. The amino group contents were determined by back titration. As expected, the amino capacity decreases as the degree of crosslinking increases (*Figure 1*).

Complexation of DVB-crosslinked aminopolyacrylamides

The complexation of amino functions supported on polyacrylamides with varying extents of DVB crosslinks was investigated for Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) ions using the batch equilibration technique. The rigid and hydrophobic DVB crosslinking exerts a striking influence on the complexation ability of the attached amino functions. The metal ion intake decreased with the extent of the DVB content (*Table 2*). The reduction in metal ion intake with increasing DVB content could arise from the increased hydrophobicity and rigidity arising from the crosslinking agents. The decreased reactivities of DVB-crosslinked polymer-supported reagents are reported in many cases[15,16]. Hg(II) has the maximum complexation in the range 0.58–3.97 meq g^{-1}. The minimum values of metal ion intakes were observed for Co(II) and Ni(II). The metal ion intake followed the order: Hg(II) $\gg$ Cu(II) > Zn(II) > Ni(II) > Co(II).

A general comparison of the Cu(II) intake and the amino capacity indicates that approximately one millimole of Cu(II) ion is complexed by one millimole of amino groups. This is an average, since the complexing availability of the ligands depends on the micro-environments around the ligand functions. The efficiency of complex formation of macromolecular ligands is influenced not only by the complexing ability of the ligands, but also by their distribution along the polymer chains. The low utilization of ligand functions in similar complexations has been reported previously[17].

Infra-red spectra

The i.r. spectrum of the DVB-crosslinked polyacrylamide showed the characteristic absorptions of amide (N–H), carbonyl and aryl groups at 3500, 1660 and 800 cm^{-1}, respectively. The N–H stretching frequencies of the Cu(II) complex are lower than those of the free amines[18]. Upon coordination, the N–H bond is weakened and the N–H stretching frequencies are lowered. The stronger the M–N bond, the weaker the N–H bond, and the lower the N–H stretching frequencies. Thus, the N–H stretching frequencies can be used as a rough measure of the M–N bond strength[19]. The N–H stretching frequencies of polyacrylamide, aminopolyacrylamide and the Cu(II) complex are given in *Figure 2*. The splitting of the broad band around 3500 cm^{-1} into two peaks, one at 3520 cm^{-1} and the other at 3440 cm^{-1}, is a clear indication for the incorporation of amino groups for coordination with metal ions preventing hydrogen bonding between the amino groups. The peak at 1650 cm^{-1} is shifted downwards by 10 cm^{-1}, indicating the incorporation of amide nitrogen for coordination. The bending at 1738 cm^{-1} and the shoulder at 1540 cm^{-1} are also not present in the complexed resin. These also indicate the involvement of the amide nitrogen in coordination with Cu(II) ions. The peak in the region 400–200 cm^{-1} is due to the Cu–N bond.

E.s.r. spectrum

The e.s.r. parameters of the Cu(II) complex of 8% DVB-crosslinked amino resin are: $g_{\parallel} = 2.3004$, $g_{\perp} = 2.0937$, $A_{\parallel} = 155$ G and $A_{\perp} = 41.667$ G. These values suggest a distorted tetragonal geometry for the Cu(II) complex[20]. For tetragonal geometry the g values are very sensitive to the nature of the ligands. The value of $g_{\parallel}$ around 2.3 suggests the covalency of the Cu–N bond.

The bonding parameter (α^2 Cu) of the complex, which is a measure of the covalency of the inplane σ-bonding of the Cu–N bond, is 0.8083 as calculated by the expression given by Kivelson and Neiman[21]. This is in the range for the covalent nature of the Cu–N bond.

Scanning electron microscopy

In this study, SEM is used to probe the change in morphological features of 8% DVB-crosslinked amino resin on complexation with Cu(II) (*Figure 3*). The SEM of the uncomplexed amino resin has a rough surface caused by the rigid and hydrophobic nature of the DVB-crosslinks. The surface morphology of the Cu(II) complexed resin is different from the uncomplexed resin. It is composed of regions of needle-like appearances. The voids present in the uncomplexed resin are not present

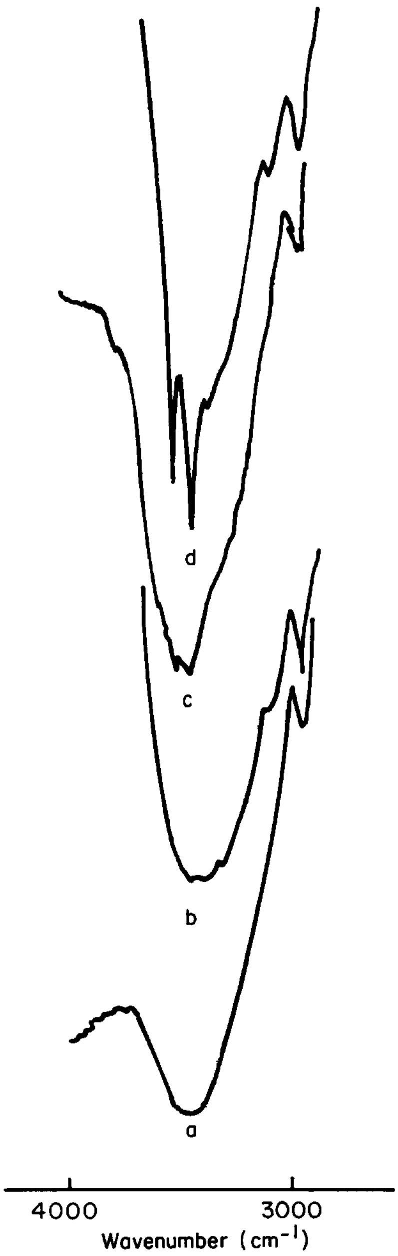


Figure 2 Infra-red absorptions of the NH_2 groups of (a) amide, (b) amine, (c) partially Cu(II) complexed resin and (d) Cu(II) complexed resin

in the complexed resin. This could arise from the contraction of the voids on complexation, or the disappearance of the voids in the rearrangement of the polymer chains for complexation with metal ions.

Thermogravimetric studies

The thermogravimetric studies of the 4% DVB-crosslinked amino resin, its complexes with Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) ions, and the Cu(II) complexes with varying extents of DVB crosslinks were carried out. The differential[22] and approximation[23] equations were applied for the mathematical analysis of the t.g. curves using the least squares method:

$$\ln g(\alpha) = \ln[AR/\phi E(1 - 2RT/E)] - E/RT \qquad (1)$$

$$\ln g(\alpha)/T = \ln[AE/\phi R] + 3.772050 - 1.921503 \ln E - 0.120394(E/T) \qquad (2)$$

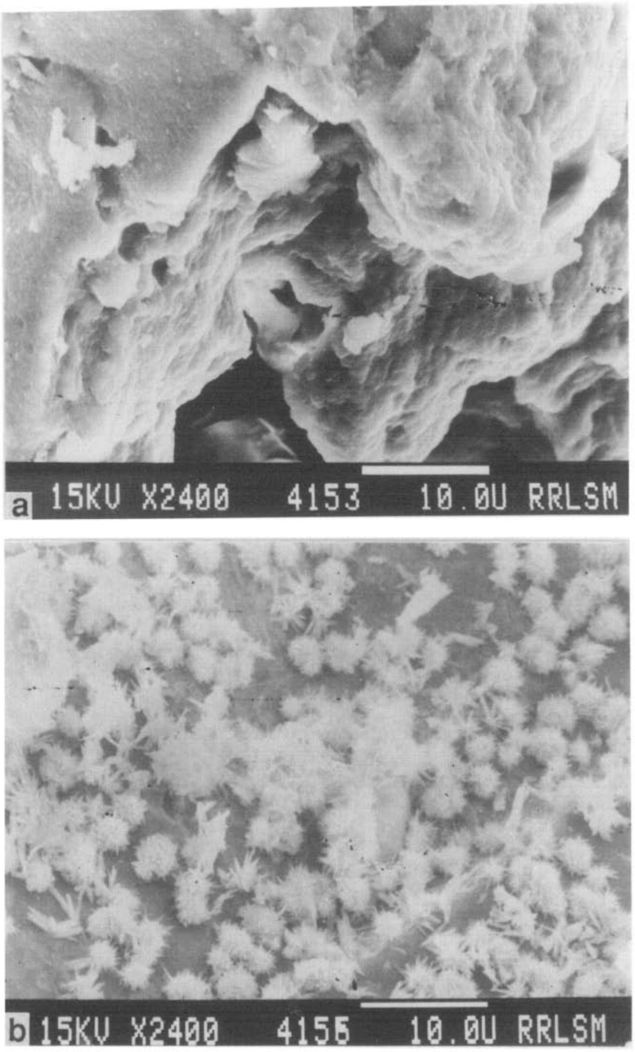


Figure 3 SEMs of (a) amine and (b) Cu(II) complexed resins with 8% DVB-crosslinking

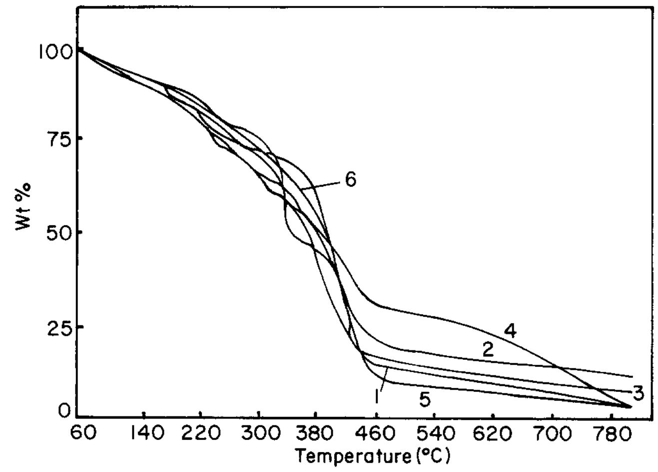


Figure 4 Thermogravimetric curves of the 4% DVB-crosslinked amino resin and metal complexes. 1: amino resin; 2: Cu(II); 3: Ni(II); 4: Zn(II); 5: Co(II); 6: Hg(II)

Metal complexes of 4% DVB-crosslinked aminopolyacrylamides. The t.g. curves of the 4% DVB-crosslinked aminopolyacrylamide and its various metal complexes are given in *Figure 4*. All the t.g. curves showed four stages of decomposition. These decompositions varied with the metal ion. The first stage decomposition is due to the removal of adsorbed or coordinated water molecules present. The second and third stage decompositions arise from the decomposition of free amide groups and uncoordinated amino groups. The last step is the major decomposition, which is used for the kinetic analysis. The kinetic data are given in *Table 4*. The activation energy for the decomposition of the amino resin is higher than that for the complexed resins. This can arise from the unsaturated coordination structure of the other metal complexes. The activation energy decreased in the order: Cu(II) > amino resin > Zn(II) > Ni(II) > Hg(II) > Co(II). The lower stabilities of the metal complexes, other than the Cu(II) complexes, are also demonstrated by the entropies of the metal complexes. There is no considerable difference between the entropies of the metal complexes and uncomplexed resin.

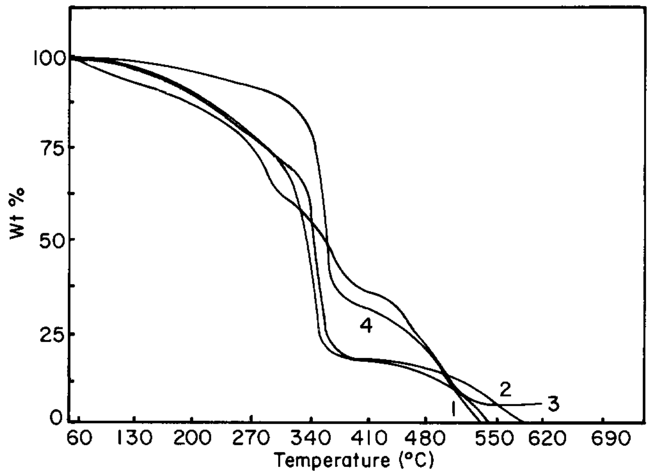


Figure 5 Thermogravimetric curves of the Cu(II) complexes with varying extents of DVB-crosslinking. 1: 2%; 2: 4%; 3: 8%; 4: 20%

Table 3 Phenomenological data of the thermal decomposition of 4% DVB-crosslinked polyacrylamide-supported amine and metal complexes

Resin/ complex	Decomposition temperature range in t.g. (K) T_i	T_f	Peak temperature in d.t.g. (K) T_s	Mass loss (%)
Amine	575	788	687	52
Co(II)	600	1007	653	51
Ni(II)	603	835	657	42
Cu(II)	561	653	612	21
Zn(II)	550	639	605	21
Hg(II)	593	1073	697	51

Cu(II) complexes with varying extents of DVB-crosslinks. The t.g. curves of the Cu(II) complexes of amino functions supported on polyacrylamides with 2, 4, 8 and 20 mol% of DVB-crosslinks are given in *Figure 5*. The t.g. curves (except for the 20% crosslinked system) have three stages. The kinetic analysis was carried out on the third stage of the 8% and 20% crosslinked systems, and the fourth stage of the 2% and 4% crosslinked systems. The kinetic data calculated by the integral and approximation methods are given in *Table 6*.

The activation energy decreases with increasing crosslinking until 8% crosslinking, and increases thereafter. The activation energy (*E*) and the extent of crosslinking (*C*) of the Cu(II) complexes fit into a cubic polynomial of the type:

$$E = a + bC + cC^2 + dC^3 \tag{3}$$

and the specific equation is:

$$E = 233.19 + 16.74612\,C - 3.6868\,C^2 + 0.1402\,C^3 \tag{4}$$

The plot of activation energy *versus* extent of crosslinking is given in *Figure 6*. The curve shows a minimum at 15% crosslinking. A fifth stage decomposition was observed in the case of the 2, 4 and 8% crosslinked systems from 522–780 K with 16–31% mass loss. The decompositions were complete in all cases, leaving the metallic oxides as the residue.

With increasing crosslinking, entropy decreases in the Cu(II) complexes. In the low crosslinked systems, complexation would occur by the cooperative contribution of the randomly distributed ligands with Cu(II) ions, which distorts the polymer chains from their normal positions. This leads to an increase in entropy. As the crosslinking increases, the concentration of the ligand functions on the polymer surface is enhanced. This appears to be due to the reduced availability of the reactive sites buried within the crosslinks for transamidation. This is validated in the highly crosslinked systems. The relatively free availability of the ligand functions on the surface of the highly crosslinked systems will make the complexation easier without introducing much strain.

Time-course and kinetics of complexation

To optimize the time required for complexation for Co(II), Ni(II), Cu(II) and Zn(II) ions, batch studies were carried out for the 4% DVB-crosslinked amino resin. The time dependence of the complexation was followed by the change in concentrations of the metal salt solutions at regular time intervals. The complexations of Co(II)

Table 4 Kinetic data of the thermal decomposition of 4% DVB-crosslinked polyacrylamide-supported amine and metal complexes

	Equation (1)				Equation (2)			
Resin/complex	E (kJ mol^{-1})	A (s^{-1})	ΔS (J)	r	E (kJ mol^{-1})	A (s^{-1})	ΔS (J)	r
Amine	141.4	8.3×10^5	−138.5	0.9983	142.3	1.5×10^6	−133.6	0.9983
Co(II)	139.1	2.0×10^5	−149.3	0.9968	139.2	3.5×10^5	−144.9	0.9969
Ni(II)	126.3	6.7×10^4	−159.3	0.9891	126.8	1.2×10^5	−154.1	0.9892
Cu(II)	141.1	3.6×10^5	−144.4	0.9928	141.5	6.5×10^5	−139.5	0.9928
Zn(II)	103.5	8.1×10^5	−195.8	0.9999	103.9	4.3×10^2	−201.0	0.9999
Hg(II)	105.0	5.9×10^2	−199.0	0.9995	105.4	1.1×10^3	−194	0.9995

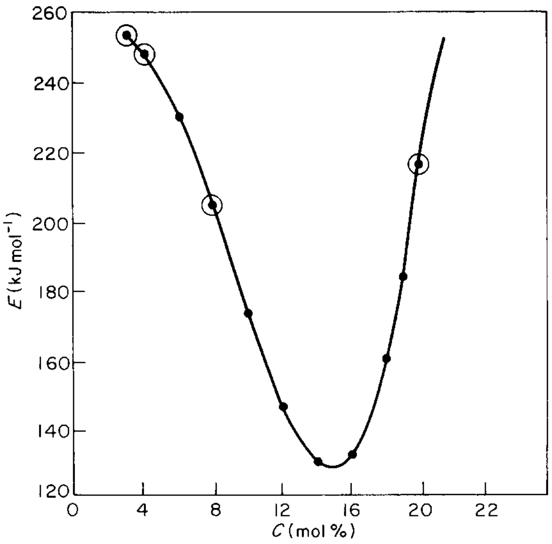


Figure 6 Activation energy *versus* extent of DVB-crosslinking. ●: Theoretical; ○: experimental

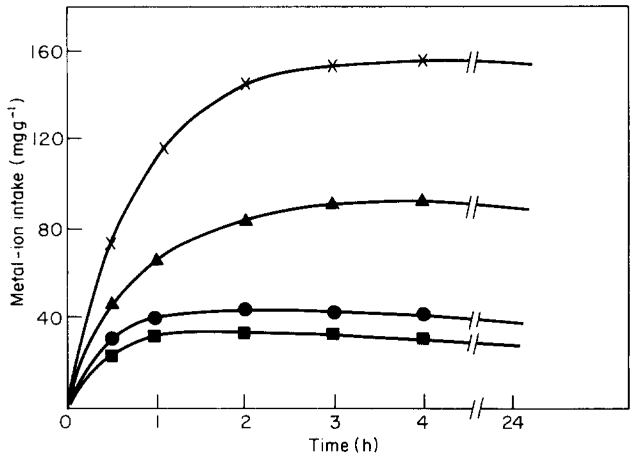


Figure 7 Time-course of metal ion intake. ×: Cu(II); ▲: Zn(II); ●: Ni(II); ■: Co(II)

and Ni(II) ions were complete in 1 h, Cu(II) in 2.5 h and Zn(II) in 3.25 h (*Figure 7*).

Kinetics of the Cu(II) complexation of the 8% DVB-crosslinked amino resin (capacity 0.5477 mmol NH_2 g^{-1}; 80–100 mesh size) was investigated. The change in concentration of the Cu(II) ions at different time intervals was followed, and the rate of reaction fits into a first order equation. The kinetics were followed at 306 K and 318 K. The rate constant at 318 K is almost double that at 306 K (*Figure 8*). The activation energy for complexation, Arrhenius parameter and the entropy of complexation are 82.410 kJ mol^{-1}, 1.15×10^9 s^{-1} and −71.63 J, respectively. These values are comparable with those obtained for solution kinetics.

Adsorption approach of complexation

In the complexation of crosslinked polymer-supported ligands with metal ions in aqueous medium, which is a heterogeneous reaction, the following fundamental processes have to be considered: (i) diffusion of metal ions into the polymer matrix; (ii) adsorption on the surface; and (iii) the reaction which may or may not be followed by desorption. In the case of adsorption, there are two possible approaches: (i) adsorption without any interaction with neighbours – Langmuir type[24]; and (ii) adsorption invoking interaction between the neighbours – Frumkin type[25]. These two possibilities are considered here.

Langmuir type. The complexation of 8% DVB-crosslinked amino resin with Cu(II) ions was carried out at different temperatures with a definite amount of the resin, and with varying concentrations of Cu(II) salt solution until equilibrium was reached. The Langmuir equation can be taken in the form:

$$C_f/C_m = \frac{1}{KA_s} + \frac{C_f}{A_s} \qquad (5)$$

where C_f is the concentration of free metal ion, C_m is the concentration of complexed metal ions, K is the adsorption constant, and A_s is the surface area covered by the metal ions. The plot of C_f/C_m against C_f is given in *Figure 9*.

The adsorption constant (K), surface area covered (A_s) and the free energy of activation (A^{Φ}) are 32.1 kJ mol^{-1}, 0.1301 and −26.4 kJ mol^{-1}, respectively, at 303 K. The adsorption parameters at 316 K are $K = 20.1$ kJ mol^{-1}, $A_s = 0.1286$ and $A^{\Phi} = -26.2$ kJ mol^{-1}. The specific rate constant decreased with temperature, whereas the surface area covered and the free energy of activation at two different temperatures are almost

Table 5 Phenomenological data of the thermal decomposition of Cu(II) complexes of polyacrylamide-supported amines with varying extent of DVB crosslinks

DVB (mol%)	Decomposition temperature range in t.g. (K) T_i	T_f	Peak temperature in d.t.g. (K) T_s	Mass loss (%)
2	360	522	420	56
4	370	522	436	54
8	304	386	356	19
20	324	510	442	60

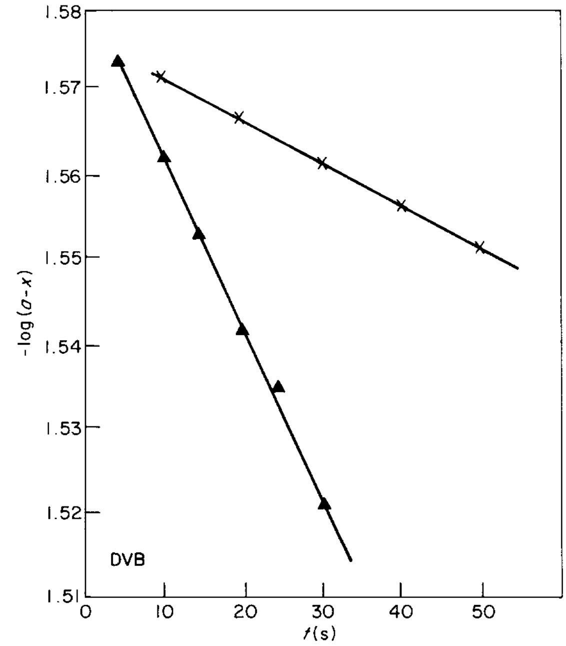


Figure 8 Kinetic curves of the Cu(II) complexation. ×: $T = 306$ K, $k_1 = 7.1 \times 10^{-6}$ s^{-1}; ▲: $T = 318$ K, $k_2 = 3.3 \times 10^{-5}$ s^{-1}

the same. This can result from the rigid nature of the DVB-crosslinked polymer-support. The kinetic parameters, activation energy of complexation/adsorption (E), Arrhenius parameter (A) and the entropy of activation (ΔS) are 31.9 kJ mol^{-1}, 8.9 × 10^9 s^{-1} and +8.3 J, respectively.

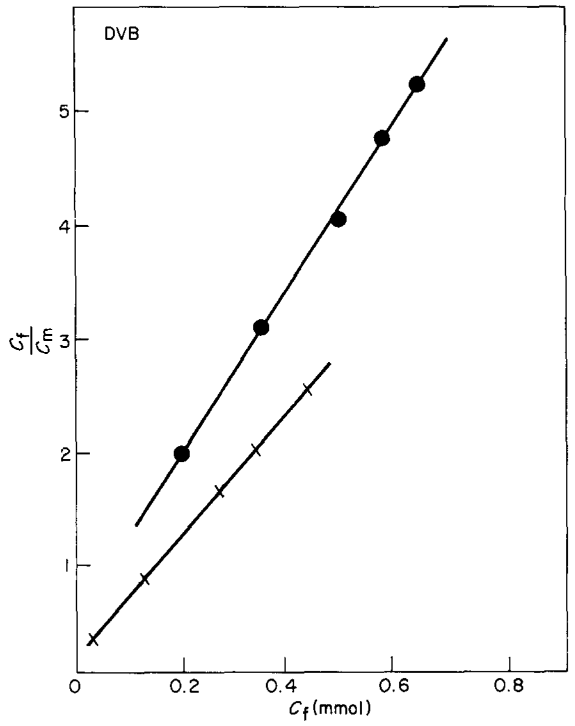


Figure 9 Langmuir plots for the Cu(II) complexation. ×: T=303 K; ●: T=316 K

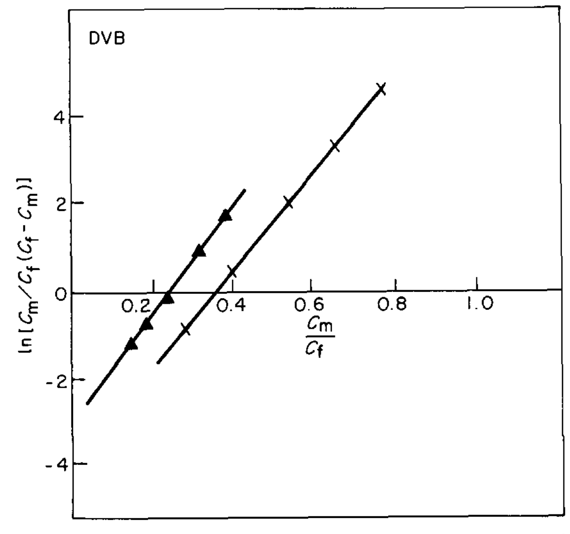


Figure 10 Frumkin plots for the Cu(II) complexation. ▲: T=316 K; +: T=303 K

Frumkin type. To investigate the interaction effect between the complexed (adsorbed) species, the Frumkin equation (6) was chosen:

$$C_f = \frac{C_m}{(C_f - C_m)K_1} e^{-K_2 C_m/C_f} \qquad (6)$$

where K_1 is the adsorption constant, and K_2 is the interaction constant. This can be transformed into:

$$\ln\left[\frac{C_m}{C_f(C_f - C_m)}\right] = \ln K_1 + K_2 \frac{C_m}{C_f} \qquad (7)$$

The experimental data obtained for the Langmuir type was also used in this case. The plots of the LHS of equation (6) *versus* C_m/C_f are given in *Figure 10*. The K_1, K_2 and the free energy of activation at different temperatures are:

$K_1 = 19.05$ kJ mol^{-1},

$K_2 = 11.08$ kJ mol^{-1}, and A^{ϕ} (adsor./interac.)

$= -25.07/-23.69$ at 303 K

$K_1 = 9.00$ kJ mol^{-1},

$K_2 = 12.16$ kJ mol^{-1}, and A^{ϕ} (adsor./interac.)

$= -24.90/-24.10$ at 316 K

The free energy of interaction is higher than the free energy of adsorption. This may be due to the possibility of increased interaction by the active sites in the rigid

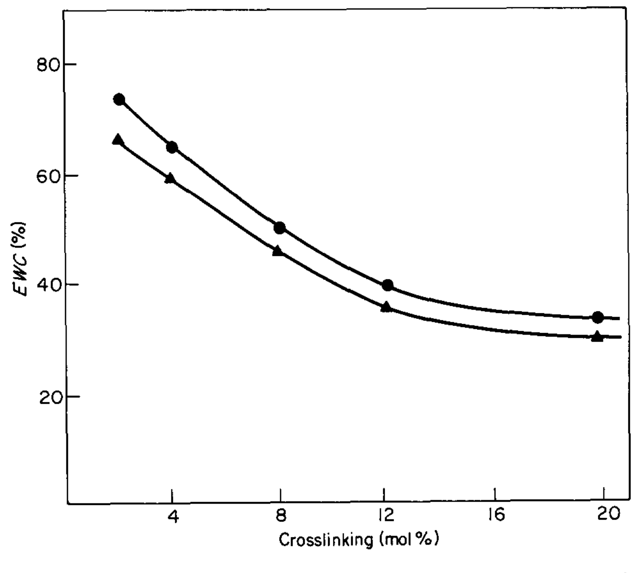


Figure 11 *EWC*s of the amino resins and Cu(II) complexes with varying extents of DVB-crosslinking. ▲: Cu(II) complexed resin; ●: uncomplexed resin

Table 6 Kinetic parameters of the thermal decomposition of Cu(II) complexes of polyacrylamide-supported amines with varying extent of DVB crosslinks

	Equation (1)				Equation (2)			
DVB (mol%)	E (kJ mol^{-1})	A (s^{-1})	ΔS (J)	r	E (kJ mol^{-1})	A (s^{-1})	ΔS (J)	r
2	253.0	2.6 × 10^{14}	+23.9	0.9964	253.5	4.7 × 10^{14}	+28.9	0.9964
4	250.2	4.2 × 10^{13}	+8.8	0.9997	250.7	7.7 × 10^{13}	+13.8	0.9996
8	203.0	2.1 × 10^{12}	−15.0	0.9957	203.4	3.9 × 10^{12}	−10.2	0.9957
20	215.1	1.2 × 10^{11}	−40.1	0.9965	216.5	2.6 × 10^{11}	−35.7	0.9968

DVB-crosslinked polymer matrix. The rigidity and hydrophobicity of the crosslinks make the active sites mainly on the surface, resulting in increased interaction. The reactive sites are almost fixed, and the swelling has no significant effect on the polymer-support. Hence the energy of activation for interaction is lower. The kinetic parameters of complexation using the Frumkin equation are $E = 6.25\ \mathrm{kJ\ mol^{-1}}$, $A = 1.3 \times 10^{-2}\ \mathrm{s^{-1}}$, and $\Delta S = -204.7$ J (*Figure 10*).

Recyclability and specificity of complexed resins

The most important advantage of chelating resins is their reuse after a particular process. The resin, once used, can be brought into its initial state by desorbing the complexed Cu(II) by 2 N sulfuric acid, and can be reused after neutralization. The 4% DVB-crosslinked amino resin with 153 mg Cu(II)/g of the resin was used in this study. The recycling of the neutralized, acid-treated resin by the addition of fresh Cu(II) solution results in the intake of almost the same amount of Cu(II) originally present. The process was repeated four times, and the results were consistent with the initial one.

To investigate the specificity of the complexed resin, four sets of 1 g each of the 4% DVB crosslinked amino resin were treated with 2 N sulfuric acid to desorb the complexed metal ions. These resins were converted to the initial stage by washing repeatedly with dilute sodium hydroxide and deionized water. They were then treated with fresh solutions of Co(II), Ni(II), Cu(II) and Zn(II), and the values of metal ion intake were followed. The intensity of the colour of the Co(II)- and Ni(II)-treated resins decreases on repeated washings. It is possible that the 'pockets' left by the Cu(II) ions may not be suited for the other metal ions, i.e. the geometry and size of the Cu(II)-desorbed resin is more suited for the Cu(II) ions than the Ni(II) and Co(II) ions. The results indicate that the Cu(II)-desorbed resin, on recycling complexed almost the same amount of Cu(II) ions. The complexation of Zn(II) was 70%, and Co(II) and Ni(II) were only 10% and 40% of the original intake. This suggests the preferred complexation of Cu(II) over the other metal ions.

The above observation was further supported by the rapid complexation of Cu(II) ions by the Cu(II)-desorbed resin. On recomplexation with Cu(II), the whole amount of Cu(II) complexed in 0.5 h whereas the fresh 4% DVB-crosslinked resin required 2.5 h for the complexation of the same amount of Cu(II). If the resin is subjected to vigorous stirring during recycling, the 'memory' of the polymer ligand or the 'pockets' fitted for the specific metal ion is disturbed, and it leads to a reduced metal intake. The same resin complexed only 83 mg Cu(II) in contrast to an original intake of 153 mg. These observations are comparable to the adjustment of the macromolecular chains of enzymes to its tertiary structure optimum for the sorption of corresponding substrate. Similar specificity of the pre-arranged sorbents have been reported[26,27].

Swelling characteristics

The complexation of a metal ion with a polymer-supported ligand which occurs in an aqueous environment is governed by the extent of swelling of the crosslinked polymer in water. In the case of crosslinked polymers, the transport of metal ions into the resin is diffusion-controlled. The extent of swelling depends on the nature and extent of the crosslinking agent. In the complexation of polymeric ligands with metal ions, the macromolecular matrix contracts by crosslinking with metal ions[28].

In the present investigation, swelling properties of aminopolyacrylamides and their Cu(II) complexes with 110 mg Cu(II) per g of the resins with 2–20 mol% of DVB crosslinks were followed. The equilibrium water content (*EWC*) values of the amino resins and their Cu(II) complexes are given in *Figure 11*. With increasing DVB content, *EWC* decreases because of the presence of rigid and hydrophobic crosslinking. Polyacrylamide itself is hydrophilic, but the introduction of DVB crosslinks imparts hydrophobicity to the extent depending on the DVB content. This is important for the reactions which are to be carried out in organic solvents. The increased reactivities of DVB-crosslinked polyacrylamides in organic solvents are reported elsewhere[12].

The *EWC*s of the Cu(II) complexes are lower than the corresponding amines. This is because of the additional crosslinking by complexation with Cu(II) ions. The reduction in swelling by complexation is in the range of 2–8%. A larger decrease is observed in the case of the low-crosslinked systems because of the further crosslinking of the extensively swollen polymer chains by complexation with Cu(II) ions. This causes the polymer matrix to contract, resulting in a decreased uptake of water. In highly crosslinked systems, the contraction of the polymer matrix is less because of the lower ligand concentration, and the ligands are distributed on the surface of the polymer matrix. This results in a lower reduction in swelling by complexation of the highly crosslinked systems.

CONCLUSION

The above investigations on the preparation of polyacrylamides with the amino functions in different structural environments, and their complexation with different metal ions, suggests that the complexation is governed by the microenvironments around the ligand functions. The i.r. absorptions of the ligand functions were shifted to lower frequencies by complexation. The mode of attachment of the ligand with the Cu(II) ion and the coordination geometry were followed from the e.s.r. spectrum. The change in the surface morphology on complexation was followed by SEM. The thermal stabilities of the metal complexes were found to be lower than the amino resin, due to the unsaturation in the coordination sphere. But the thermal stabilities of the Cu(II) complexes are higher than the amino resins, and the activation energy values fit into the general equation for a cubic polynomial. The kinetics of complexation was found to be first order. The complexed resins can be recycled several times, and the metal desorbed resin selectively binds the desorbed metal ions. The swelling characteristics decreased with increasing crosslinking, and the swelling is generally lower for the complexed resin.

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