

Metal ion complexation of hydrophilic polymeric amino ligands derived from tetraethyleneglycol diacrylate (TTEGDA)-crosslinked polyacrylamides

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Abstract. Complexation behaviour of amino ligands supported on polyacrylamides with 2–20 mol% of tetraethyleneglycol diacrylate crosslinks was investigated towards Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) ions. The metal ion intake was dependent on the extent of crosslinking and followed the order: Hg(II) > Cu(II) > Zn(II) > Ni(II) > Co(II). The aminopolyacrylamides and their metal complexes were characterised by IR and EPR techniques. The absorptions of the ligands were shifted by complexation with metal ions and the EPR spectrum suggested distorted tetragonal geometry for the Cu(II) complex. The thermogravimetric analysis of the metal complexes revealed a pattern of variation of thermal stability on incorporation of metal ions. The kinetics and adsorption parameters of complexation, swelling characteristics, recyclability and specificity of metal-desorbed systems are also described.

Keywords. Polymer–metal complexes; crosslinked polyacrylamides; amine–metal complexes; specificity.

1. Introduction

The study of polymer–metal complexes is relevant in the areas of catalysis, metal ion separation and bioinorganic chemistry (Warshawsky 1988; Ciardelli *et al* 1994). In a polymer-supported ligand, the ligand function is only an infinitesimal part of the three-dimensional polymer matrix (Drago and Gaul 1979; Green and Hancock 1981; Nishide *et al* 1982). The progress achieved in the synthetic methodology of polymers and in the area of their structure–reactivity correlations permits one to obtain macromolecular matrices of well-defined characteristics. Chemical reactions for the introduction of functional groups and functional group conversion in polymers are also dependent on the characteristics of the macromolecular support (Pillai and Mathew 1993). The nature of the monomers, degree of crosslinking, and separation of the ligand function from the polymer support are important in deciding the complexation characteristics of the polymer supported ligands.

This paper describes (i) the preparation of polyacrylamides with 2–20 mol% of hydrophilic and flexible tetraethyleneglycol diacrylate (TTEGDA) crosslinks; (ii) incorporation of amino ligands; (iii) correlation of the extent of crosslinking with complexation of Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) ions; (iv) physicochemical

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characterisation of the derived metal complexes; and (v) recyclability and specificity of the complexed resins.

2. Experimental

2.1 General

All the reagents were of certified ACS reagent grade. The purest available metal salts were used to prepare metal ion solutions. The IR spectra were recorded on a Perkin-Elmer 983 IR spectrophotometer using KBr pellets. The EPR spectrum was recorded on a Varian E-12 instrument at room temperature. TG curves were recorded on a Delta Series TGA-7 thermal analyser at a heating rate of $20^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere.

2.2 Synthesis of tetraethyleneglycol diacrylate (TTEGDA)-crosslinked polyacrylamides

TTEGDA-crosslinked polyacrylamides were prepared by redox copolymerization of the monomers. TTEGDA was washed with sodium hydroxide solution (1%) and with water to remove the inhibitor. The mixture of the monomers was dissolved in ethanol (70 ml). Ammonium persulphate (100 mg) was added to it and the contents were heated on a water-bath at 60°C . The mixture was stirred until the polymer precipitated. Heating was continued for 30 min more and the polymer filtered, washed with water and methanol and dried at 70°C . Polyacrylamides with varying extents of TTEGDA crosslinks were prepared by varying the composition of the monomers in the feed.

2.3 Transamidation of TTEGDA-crosslinked polyacrylamides with ethylenediamine

Polyacrylamide (10 g) and ethylenediamine (100 ml) were heated together with stirring for 9 h at 100°C . The reaction mixture was filtered and washed with NaCl solution (0.1 M) until the filtrate was free from ethylenediamine, as indicated by the absence of blue colouration with ninhydrin reagent. The gel was washed with water to remove NaCl and then with methanol and dried at 70°C .

2.4 Estimation of resin amine content

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

2.5 Complexation of metal ions with amino resins

200 mg each of the resin samples was stirred with metal salt solution (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 the metal salt solutions were estimated by volumetric methods: Cu(II) by iodometry, Ni(II) and Zn(II) by complexometry and Co(II) and Hg(II) by back-titration using complexometric methods.

2.6 Time-course of complexation

Batch studies were carried out with 500 mg of 4% TTEGDA-crosslinked amino resin. Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) solutions (100 ml each) were added to the amino resins and stirred. At regular intervals, 2 ml aliquots were withdrawn from the test solution and estimated.

2.7 Kinetics of complexation

Different sets of 8% TTEGDA-crosslinked amino resin (100 mg) were stirred with Cu(II) salt solution (6.5×10^{-3} N, 100 ml) at room temperature (303 K) and at 290 K in a thermostatically controlled system for varying time intervals. The remaining concentration of Cu(II) ions in each case was estimated.

2.8 Adsorption studies

Different sets of 100 mg of 8% TTEGDA-crosslinked amino resin were equilibrated with Cu(II) salt solution of varying concentrations at two different temperatures (303 K and 290 K). Temperature of complexation/adsorption was kept constant using a thermostat. Langmuir and Frumkin equations were used for the adsorption studies.

2.9 Swelling studies

500 mg each of the amino resins was equilibrated with 30 ml distilled water for 48 h. The swollen resins were collected by filtration, adhering traces of water were removed by pressing with filter paper, and the resins weighed. They were then dried in vacuum for 24 h and weighed again. Another set of the resins was equilibrated with 30 ml cupric sulphate solution containing 0.66 meq copper(II) and weights of the wet and dried resins were measured. From the swollen and dried weights of the samples the equilibrium water content (EWC) (%) was calculated using the equation:

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

2.10 Recyclability and specificity studies

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

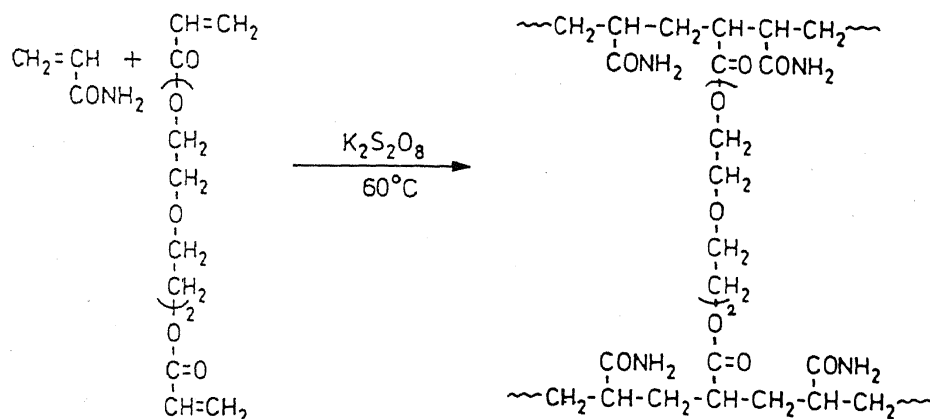
3. Results and discussion

3.1 Preparation of 2–20 mol% TTEGDA-crosslinked polyacrylamide-supported amines

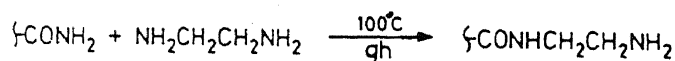
Polyacrylamides with varying extents of TTEGDA crosslinks were prepared by solution polymerization of the monomers in ethanol using potassium persulphate as the initiator (scheme 1). The introduction of hydrophilic and flexible TTEGDA crosslinks made the polymer gels soft and sticky. When TTEGDA content increased, the rigidity increased and the swelling in water also varied.

Transamidation reactions of polyacrylamides with low molecular weight amines were used for the preparation of amino functional polymers (Inman and Dintziz 1969). In the transamidation of TTEGDA-crosslinked polyacrylamides, ethylenediamine itself was used as the solvent and the reaction was carried out at 100°C (scheme 2).

Amino functions were detected by the semi-quantitative ninhydrin reaction (Sarin *et al* 1981). The resins developed a deep blue colour with the ninhydrin reagent. The amino capacities are 2% – 5.526; 4% – 3.584%; 8% – 4.149; 12% – 4.340; 20% – 4.36 meq/g. The amino capacities of the resins decreased till 4% crosslinking and increased further. In the preparation of amidoxime derivatives of acrylonitrile-oligoethyleneglycol dimethacrylate copolymers, with varying ethyleneglycol units,



Scheme 1. Preparation of TTEGDA-crosslinked polyacrylamide.



Scheme 2. Transamidation of TTEGDA-crosslinked polyacrylamide with ethylenediamine.

Table 1. Metal ion intake by TTEGDA-crosslinked aminopolyacrylamides.

TTEGDA (mol%)	Metal ion intake (meq.g ⁻¹)				
	Co(II)	Ni(II)	Cu(II)	Zn(II)	Hg(II)
2	0.97	1.67	3.29	1.91	4.96
4	0.59	0.68	2.97	0.83	2.60
8	0.59	0.80	0.90	1.82	3.18
12	0.59	0.99	2.79	2.23	3.94
20	0.59	1.19	2.77	2.33	4.19

hydrolytic cleavage of the crosslinks in basic medium has been observed (Egawa *et al* 1988). In the case of TTEGDA-crosslinked amino resin, the increase in amino capacities with increasing crosslinking originates from the additional contribution of amino groups resulting from the hydrolysis of the ester linkages in the crosslinking. This increases with increasing amount of the crosslinking agent in the polymer matrix. The swelling properties also suggest the cleavage of considerable number of ester groups from 8% crosslinking onwards.

3.2 Complexation of TTEGDA-crosslinked aminopolyacrylamides

The complexation of amino functions supported on polyacrylamides with varying extents of TTEGDA crosslinks was investigated for Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) ions by batch equilibration technique at their natural pH. For all the metal ions, the complexation was maximum for the 2% crosslinked resin. The metal ion intake for the 4% crosslinked resin was lower and it increased further (table 1). The metal ion intake followed the order: Hg(II) > Cu(II) > Zn(II) > Ni(II) > Co(II).

The complexation characteristics of the Cu(II) and Co(II) ions were found to be independent of the extent of crosslinking after 4%. For other metal ions, however, the variation of complexation with extent of crosslinking is more significant. This variation is related to the amino capacities of the crosslinked polymers. The complexation is much lower for Co(II). For Hg(II), Zn(II) and Ni(II), the complexation increases after 4% crosslinking. The increase in metal ion complexation after 4% crosslinking arises from the increased amino capacity and availability of the ligands resulting from the partial aminolysis of the ester units in the crosslinks. Similar observations of the increase in reactivity with increase in TTEGDA crosslinks have been reported in the case of polyacrylamide supported reagents (Chandy and Pillai 1991).

3.3 Infrared spectra

The IR spectrum of the crosslinked polyacrylamide showed the characteristic absorption of C=O at 1660 cm^{-1} . This is overlapped with the bending mode of the N-H band. The peak at 1445 cm^{-1} is the C-N stretch of the amide group. The absorption at 1100 cm^{-1} corresponds to the ether units in the TTEGDA crosslinks. In the case of the amino resin, the broad N-H peak centred around 3500 cm^{-1} appears to be an indication of the high degree of hydrogen bonding. The shoulder at 1638 cm^{-1} is the N-H bending of the NH_2 group. The absorption between 1590 and 1500 cm^{-1} is characteristic of the secondary amide groups by transamidation with ethylenediamine. The N-H stretching frequencies of the Cu(II) complexes are lower than those of the free amines by the weakening of bond (Fujita *et al* 1956). 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} and shifting of the peak at 1650 cm^{-1} by 10 cm^{-1} downwards indicated the incorporation of the amido amide nitrogen for coordination. The peak in the region $400\text{--}200\text{ cm}^{-1}$ corresponds to the Cu-N bond.

3.4 EPR spectrum

The EPR parameters of the 8% TTEGDA-crosslinked amine-Cu(II) complex are: $g_{\parallel} = 2.294$, $g_{\perp} = 2.089$, $A_{\parallel} = 160\text{ G}$, $A_{\perp} = 4.6\text{ G}$. These values suggest the distorted tetragonal geometry of the Cu(II) complexes (Peisach and Blumberg 1974). The

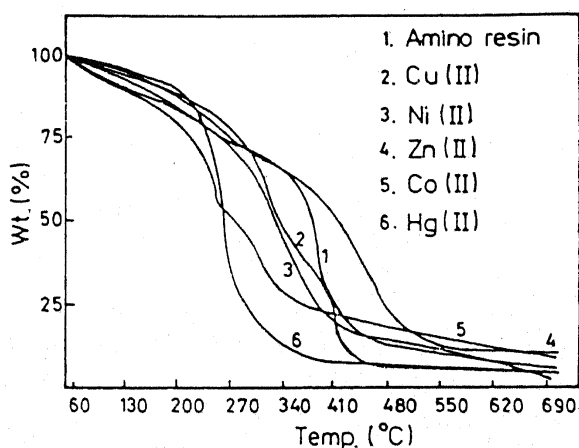


Figure 1. TG curves of 2% TTEGDA-crosslinked aminopolyacrylamide and metal complexes.

Table 2. Phenomenological data of thermal decompositions of 2% TTEGDA-crosslinked polyacrylamide-supported amine and metal complexes.

Resin Complex	Decomposition temp. range in TG (K)		Peak temp. in DTG (K)	Mass loss (%)
	T_i	T_f	T_s	
Amine	562	1017	665	67
Co(II)	513	625	520	31
Ni(II)	532	815	599	45
Cu(II)	566	653	596	26
Zn(II)	589	828	668	49
Hg(II)	497	1102	605	85

T_i - Initial decomposition temperature for the analysed stage in the thermogravimetric (TG) curve

T_f - Final decomposition temperature for the analysed stage in the TG curve

T_s - Peak temperature in the derivative thermogravimetric (DTG) curve

bonding parameter ($\alpha^2\text{Cu}$) which is a measure of the covalency of the Cu-N bond is found to be 0.8138 (Kivelson and Neiman 1961).

3.5 Thermogravimetric study of the complexes

The TG studies of the 2% TTEGDA-crosslinked amino resin and its complexes with Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) ions are given in figure 1. All the TG curves showed mass losses in the range 4–14% up to 482 K. This is attributed to the loss of adsorbed and/or coordinated water molecules present in the complexes. The second stage is the slow decomposition of unfunctionalised amide groups as well as the free ligands present in the complexes. This stage occurs in the temperature range 445–624 K with mass losses in the range 3–19%. The third stage is the major decomposition and this is used for the kinetic analysis. The phenomenological data of this stage for different systems are given in table 2.

The kinetic analysis of the TG curves was carried out using the integral (1) and approximation (2) equations using the least squares method (Coats and Redfern 1964; Madhusudanan *et al* 1986).

$$\log g(x)/T^2 = \log [AR/\phi E(1 - 2RT/E) - E/2.303RT], \quad (1)$$

$$\log g(x)/T^{1.921503} = \log AE/\phi R + 8.68703 - 1.921503 \log E - 0.120394(E/T). \quad (2)$$

The kinetic parameters are given in table 3. The activation energy decreased in the order: Cu(II) > amino resin > Ni(II) > Co(II) > Hg(II) > Zn(II). The lower stabilities of the metal complexes other than that of the Cu(II) complex appear to be due to the unsaturation in the coordination geometry.

The entropy of the Cu(II) complex is much higher than those of the uncomplexed resins and the other metal complexes. This also points to the higher thermal stability of the Cu(II) complex owing to the complete coordination sphere. For other metal ions

Table 3. Kinetic data of the thermal decompositions of 2% TTEGDA-crosslinked polyacrylamide-supported amines and metal complexes.

Resin/ Complex	Equation (1)					Equation (2)				
	E (kJ mol ⁻¹)	A (s ⁻¹)	ΔS (J)	r ($\times 10^{-1}$)	E (kJ mol ⁻¹)	A (s ⁻¹)	ΔS (J)	r ($\times 10^{-1}$)		
Amine	140.3	9.5×10^5	-137.2	9.938	140.8	2.4×10^6	-132.3	9.996		
Co(II)	120.6	8.0×10^5	-136.5	9.984	121.0	1.4×10^6	-131.7	9.984		
Ni(II)	139.6	2.6×10^7	-108.6	9.989	140.0	4.7×10^7	-103.8	9.989		
Cu(II)	252.5	4.9×10^{17}	+88.0	9.995	252.9	8.7×10^{17}	+93.8	9.989		
Zn(II)	83.3	1.3×10	-230.2	9.968	85.1	3.2×10	-222.9	9.969		
Hg(II)	104.5	2.0×10^4	-168.5	9.979	104.9	3.6×10^4	-163.6	9.979		

r - Correlation coefficient

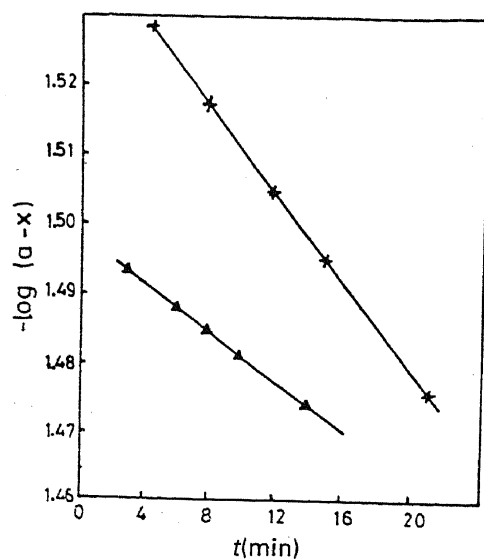


Figure 2. Kinetic curves for the Cu(II) complexation of 8% TTEGDA-crosslinked aminopolyacrylamide. (x - temp. = 290 K, $k_1 = 5.1 \times 10^{-5} \text{ s}^{-1}$; ▲ - temp. = 303 K, $k_2 = 2.8 \times 10^{-5} \text{ s}^{-1}$.)

the entropies are more or less the same as the uncomplexed resins, suggesting the decreased rearrangement of the polymer chains for complexation with metal ions which in turn leads to the development of unsaturated coordination structure.

3.6 Time-course and kinetics of complexation

The time dependence on the complexation of TTEGDA-crosslinked amino resin towards various metal ions was followed by the change in concentration of the metal salt solution at regular intervals of time. The complexation of the Co(II) and Ni(II) ions was complete in 0.5 h whereas the Cu(II) and Zn(II) complexation required 1.25 h and 2 h respectively. The rapid complexation in the case of these polyacrylamide-supported amines is because of the increased local concentration of ligands as well as the hydrophilic nature of the polymer support. The hydrophilic nature of the polymer support increases the accessibility of the ligands for complexation with metal ions.

Kinetics of the complexation of Cu(II) ions with aminopolyacrylamides with 8% TTEGDA crosslinking ($1.1075 \text{ mmol NH}_2 \text{ g}^{-1}$) of the resin (80–100 mesh) was investigated. The change in concentration of Cu(II) ions was followed by determining the concentration of Cu(II) ions at regular intervals of time and the rates of reaction fit into first order kinetics (figure 2). Because of the rapid complexation, the kinetics were followed at room temperature (303 K) and at a lower temperature (290 K). The specific rate constant at higher temperature was found to be less in the case of TTEGDA-crosslinked resins. The exothermicity of the complexation process and the dissociation of the complex leads to an overall decrease in the rate.

3.7 Adsorption approach to complexation

In the complexation of crosslinked polymer-supported ligands with metal ions, 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

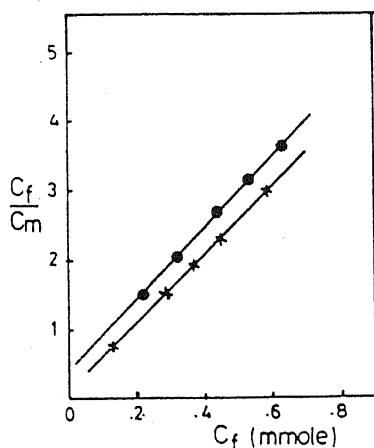


Figure 3. Langmuir plots for the copper intake by 8% TTEGDA crosslinking. ($T = 303\text{ K}$ (\times), 290 K (\bullet)).

adsorption, there are two possible approaches: (i) adsorption without any interaction with neighbours – Langmuir type (Laidler 1986); and (ii) adsorption invoking interaction between neighbours – Frumkin type (Adamson 1990). These two possibilities are considered here.

Langmuir type

In the Cu(II) complexation/adsorption of 8% TTEGDA-crosslinked aminopolyacrylamide, the Langmuir equation can be taken in the form:

$$C_f/C_m = 1/K A_s + C_f/A_s,$$

where C_f and C_m are the concentrations of free and 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 3. The activation energy for complexation in this case is 88.8 kJ mol^{-1} . The adsorption parameter is $2.2 \times 10^{20}\text{ s}^{-1}$ and the entropy of activation is -225.5 J . The adsorption parameters at 290 K are: $K = 22.5\text{ kJ mol}^{-1}$; $A_s = 0.1740$ and $A^\phi = -36.2\text{ kJ mol}^{-1}$ and at 303 K are: $K = 109.3\text{ kJ mol}^{-1}$; $A_s = 0.1960$ and $A^\phi = -96.5\text{ kJ mol}^{-1}$.

The higher energy of activation, specific rate constant and the greater negative value of free energy of activation support the view that increased complexation can occur at higher temperature. With increase in temperature, the latent reactive sites in the possibly coiled crosslinks become more exposed, thereby enhancing the complexation. The entropy of activation at higher temperature delineates the disordering of the ordered structure of the polymer matrix. This results from increased diffusion of the solvent into the crosslinks, uncoiling them and leading to increased complexation. The surface area covered by Cu(II) ions at 290 K is 17.4% and at higher temperature is 19.6% .

Frumkin type

In order to investigate the interaction effect in complexation, the Frumkin equation was chosen

$$C_f = C_m / (C_f - C_m) K_1 e^{-K_2 C_m / C_f}$$

where K_1 and K_2 are constants. This can be transformed into

$$\ln[C_m / C_f (C_f - C_m)] = \ln K_1 + K_2 C_m / C_f$$

The experimental data obtained for the Langmuir type were used in this case also. The plots of the LHS of the above equation vs C_m/C_f at different temperatures are given in figure 4. The kinetic parameters of interaction are $E = 2.3 \text{ kJ mol}^{-1}$; $A = 24 \text{ s}^{-1}$ and $\Delta S = -218.6 \text{ J}$. The adsorption/interaction parameters at 290 K are: $K_1 = 2.3 \text{ kJ mol}^{-1}$; $K_2 = 9.7 \text{ kJ mol}^{-1}$ and $A^\phi(\text{ads/int}) = -18.6/-22.1$ and at 303 K: $K_1 = 3.2 \text{ kJ mol}^{-1}$; $K_2 = 10.1 \text{ kJ mol}^{-1}$ and $A^\phi(\text{ads/int}) = -20.3/-23.2$. The activation energy for interaction is very low because of the extensively swollen polymer matrix. The free energy of interaction is lower than the free energy of adsorption. This arises from the flexibility of the crosslinking agent.

3.8 Swelling characteristics

In the present study, swelling characteristics of the aminopolyacrylamides with varying extents of TTEGDA crosslinks and their Cu(II) complexes with definite amounts of Cu(II) were followed (figure 5). To follow the change in swelling by the breaking of the crosslinking agent, the swellings of the TTEGDA crosslinked polyacrylamides with

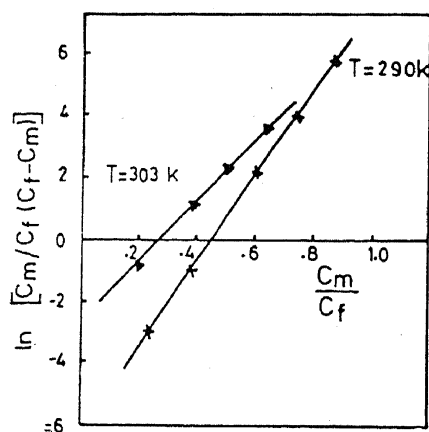


Figure 4. Frumkin plots for the copper intake by TTEGDA crosslinking.

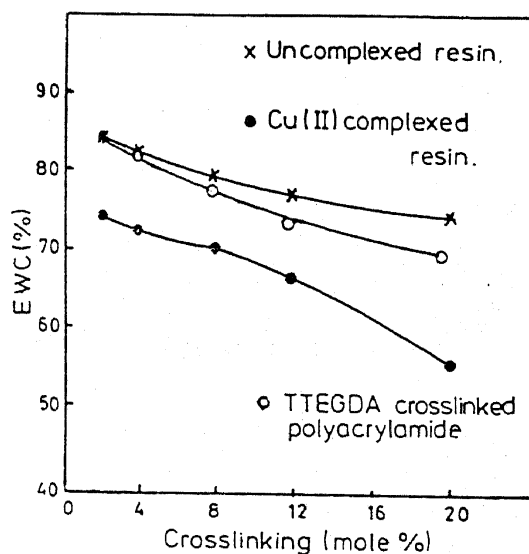


Figure 5. EWCs of the TTEGDA-crosslinked polyacrylamides, aminopolyacrylamides and Cu(II) complexes.

2–20 mol% of crosslinking were also investigated. The EWC of the 2% crosslinked system is higher because of the low content of the crosslinking and the hydrophilic nature of the crosslinks. The EWC values of the 8–20% crosslinked amino resins are higher than the corresponding polyacrylamide resins while those of the 2 and 4% crosslinked resins remained almost the same. This is because of the rupturing of the ester linkages in the crosslinking agent. The values of the EWC for the complexed resins are lower than those of the amino resins. The complexation with Cu(II) ions imparts additional crosslinking in the matrix resulting in decreased swelling (Welleman *et al* 1981). The difference in the swelling properties of the amino and Cu(II) complexed resin is higher for the 8–20 mol% crosslinked resins. This significant decrease after 4% crosslinking appears to originate from the cleavage of the crosslinking agent and the increase in swelling after the transamidation step. The tight coiling of the loosely connected chains by inter-chain chelation with Cu(II) ion causes relatively low swelling only.

3.9 Recyclability and specificity of complexed resins

In order to investigate the recyclability of TTEGDA-crosslinked aminopolyacrylamide, the Cu(II) complex of 4% TTEGDA-crosslinked aminopolyacrylamide was desorbed using dilute acid. The acid-treated and neutralized resin complexed almost to the same extent with Cu(II) as the original resin. The retention of the initial capacity even after four cycles of repeated operations suggests that the resin can be used several times without reduction in capacity. These Cu(II) desorbed resins on treatment with fresh solutions of Co(II), Ni(II), Cu(II) and Zn(II) ions specifically bind copper rather than other metal ions. The extents of complexation in the case of Zn(II), Co(II) and Ni(II) are 70%, 10% and 30% of the original metal ion binding. This is also supported by the rapid complexation of Cu(II) by the copper-desorbed system. During recycling, if the resin is subjected to vigorous stirring, the metal ion intake is reduced to half of the original value. Similar specificity of the pre-arranged sorbents has been reported (Nishide *et al* 1977).

4. Conclusion

The foregoing study on the preparation of aminopolyacrylamides and their complexation with various metal ions suggests that the complexation is governed by the microenvironment around the ligand functions. The IR absorptions of the ligand functions shift on complexation, while the EPR parameters suggest the distorted tetragonal geometry of the Cu(II) complex. The thermal stabilities vary on incorporation of metal ions. Swelling characteristics depend on functionalization and decrease on complexation. The resin can be recycled several times; the metal-desorbed resin selectively binds the metal ion which was initially present.

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