

N,N'-Methylene-bis-acrylamide-Crosslinked Polyacrylamides as Supports for Dithiocarbamate Ligands for Metal Ion Complexation

Beena Mathew & V. N. Rajasekharan Pillai*

School of Chemical Sciences, Mahatma Gandhi University, Kottayam, Kerala—686631, India

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Abstract: The complexation behaviour of dithiocarbamate functions supported on polyacrylamides with varying extents (2–20 mol%) of *N,N'*-methylene-bis-acrylamide (NNMBA) crosslinks was investigated. The crosslinked polyacrylamides were prepared by the free radical solution polymerization of the monomers in water at 80°C using potassium persulphate as initiator. The dithiocarbamate ligands were introduced by polymer-analogous reaction involving transamidation with ethylenediamine and dithiocarbamylation with carbon disulphide and alkali. The complexation behaviour of these dithiocarbamate resins with the ligand functions in different macromolecular environments were investigated towards Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) ions by a batch equilibration technique. The metal ion intake varied with the extent of the NNMBA-crosslinking. Thus the 8% crosslinked system has the highest complexation capacity. The values for metal ion intake followed the order Hg(II) >> Cu(II) > Zn(II) > Ni(II) > Co(II). The time-course of complexation, the possibility of recycling and the swelling characteristics of the uncomplexed and complexed resins were considered, and IR characterization and thermal studies were undertaken. The swelling values of the complexed resins are lower than those of the uncomplexed resins. The thermal stability of dithiocarbamates varied with the extent of NNMBA-crosslinks and with the metal ion.

Key words: polymer–metal complexes, crosslinked polyacrylamide-support, dithiocarbamate–metal complexes, thermal stability.

1 INTRODUCTION

In recent years there has been increased interest in the metal complexation behaviour of polymer-supported ligands as analytical reagents, catalysts and in pollution control.^{1–4} The complexation behaviour of a polymer-supported ligand is different from that of the corresponding low-molecular weight analogue, as a result of a number of factors characteristic of the polymer-support. In a polymer-supported ligand, the ligand function is only an infinitesimal part of the three-dimensional macromolecular matrix. Hence the complexation parameters of the polymeric ligand are decided by the polymer matrix and are governed by the nature of the polymer backbone,

the nature and extent of the crosslinking agent, and the separation of the ligand function from the polymer matrix.^{5–8} The correlation of these factors with the reactivity of attached functional groups forms the basis of the recent developments in the chemistry of functional and speciality polymers.^{9–14}

Dithiocarbamates form a group of sulphur-containing ligands with application in analytical and biological fields.^{15–17} They have been widely used for the collection of heavy metal ions from aqueous solutions, with the notable exception of alkali and alkaline earth metal ions.¹⁸ The present paper describes the complexation behaviour of dithiocarbamate functions supported on polyacrylamides with 2–20 mol% of *N,N'*-methylene-bis-acrylamide (NNMBA) crosslinks. The ligand functions were introduced by a two-step polymer-analogous

* To whom all correspondence should be addressed.

reaction involving (1) transamidation of polyacrylamides with ethylenediamine to aminopolyacrylamides and (2) dithiocarbamylation of the aminopolyacrylamides with carbon disulphide and alkali. The complexations of the functionalized resins with the ligand functions in different structural environments were investigated for metal ions such as Co(II), Ni(II), Cu(II), Zn(II) and Hg(II). The time-course of complexation, the swelling characteristics of the uncomplexed and complexed resins, recyclability of the complexed resins and the IR characterization of the polymer ligand and metal complexes are detailed in this paper. The change in the surface morphology of the polymeric ligands by complexation is followed by scanning electron microscopy. Thermogravimetric studies of the Cu(II) and Ni(II) complexes with varying extents of NNMBA-crosslinks are also described.

2 EXPERIMENTAL

2.1 General

All the reagents were of analytical grades. The purest available metal salts were used to prepare metal ion solutions. The IR spectra were recorded on a Perkin-Elmer 983 IR Spectrophotometer. Thermograms were recorded on a Delta Series TGA-7 Thermal Analyser at a heating rate of $20^{\circ}\text{C min}^{-1}$ in nitrogen atmosphere, and scanning electron micrographs were recorded on a Jeol JSM 35C microscope.

2.2 Synthesis of (NNMBA)-crosslinked polyacrylamides

NNMBA-crosslinked polyacrylamides were prepared by free radical solution polymerization of the monomers in water. For the preparation of 2% NNMBA-crosslinked polymer, acrylamide (14.0 g) and NNMBA (0.6 g) were dissolved in water (100 ml). Potassium persulphate (100 mg) was added and the mixture was heated at 80°C with stirring until the polymer precipitated. Water (80 ml) was added and the mixture again heated at 80°C for 30 min. The lumps were powdered, washed with water, ethanol and methanol, and dried at 70°C . Polyacrylamides with 4, 8, 12 and 20 mol% of NNMBA-crosslinks were prepared by varying the mol% of the monomers in the feed.

2.3 Transamidation of NNMBA-crosslinked polyacrylamides: preparation of poly(N-2-aminoethylacrylamide)s

Ethylenediamine (100 ml) was added to well-stirred polyacrylamide (10 g). The mixture was heated at 100°C for 9 h and the reaction mixture was poured into water (1 litre) containing crushed ice. The resin was filtered, washed with sodium chloride solution (0.1M) until the washings were free from ethylenediamine, as indicated by

the absence of any blue coloration with ninhydrin reagent. The gel was washed with water to remove sodium chloride, and with methanol, and dried at 70°C .

2.4 Estimation of resin amine content

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

2.5 Dithiocarbamylation of poly(N-2-aminoethylacrylamide)s

Aminopolyacrylamide (5 g) was suspended in a five-fold molar excess (calculated on the basis of amino capacity) of carbon disulphide and sodium hydroxide in water (50 ml) and shaken in a mechanical shaker for 9 h. The resin was collected by filtration, washed with water until the washings were free from sodium hydroxide, and finally washed with methanol and dried in vacuum.

2.6 Complexation of metal ions with the dithiocarbamate resins

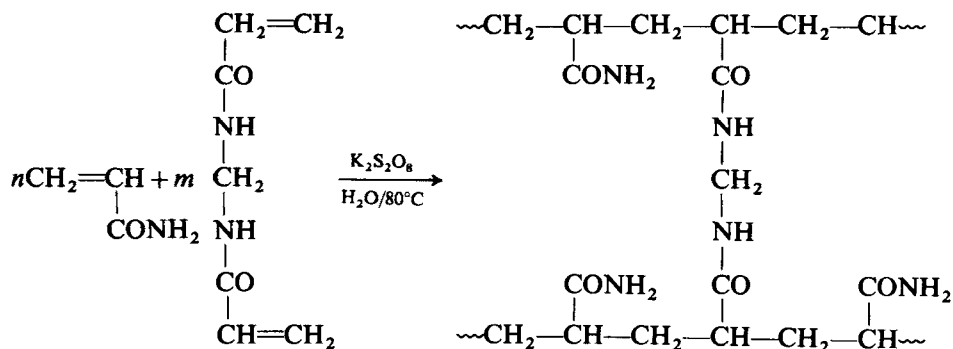
The complexation of dithiocarbamate resins with varying extents of NNMBA-crosslinks was carried out with Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) ions by a batch equilibration method. Each of the resin samples (200 mg) was stirred with a definite concentration of excess metal salt solution (0.03N, 50 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 volumetrically; Cu(II) by iodometry, Ni(II) and Zn(II) by complexometry, and Co(II) and Hg(II) by back-titration using complexometric methods. The results were then re-evaluated to obtain the standard expression of metal ion intake per gram of the resin.

2.7 Time-course of complexation

Batch studies were carried out with 500 mg of the 4% NNMBA-crosslinked dithiocarbamate resin to find the optimum time required for maximum complexation. Co(II), Ni(II), Cu(II) and Zn(II) solutions (100 ml each) were added to the dithiocarbamate resin and stirred. Aliquots (2 ml) were withdrawn at regular intervals from the test solution and estimated.

2.8 Recyclability of the complexed dithiocarbamate resin

Cu(II) complexed dithiocarbamate resin (4% crosslinked, 1 g) was stirred with nitric acid (3N, 15 ml) for 2 h. The



Scheme 1. Preparation of NNMBA-crosslinked polyacrylamides.

desorbed metal ions were collected by washing with distilled water, and were estimated iodometrically. The resin left after the treatment with nitric acid was washed with sodium hydroxide and distilled water, and again subjected to dithiocarbamylation and complexation.

2.9 Swelling characteristics

Each of the dithiocarbamate resins (500 mg) was equilibrated with 30 ml of distilled water for 48 h. The swollen resins were collected by filtration, traces of water adhering were removed by pressing with filter paper, and the resins were weighed. The swollen resins were dried in vacuum for 24 h and each of the resins was equilibrated with 30 ml of copper salt solution containing 55 mg of Cu(II) ion and the swelling measurements were carried out similarly. From the swollen and dry weights of the samples the equilibrium water content (EWC) was calculated using the expression

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

3 RESULTS AND DISCUSSION

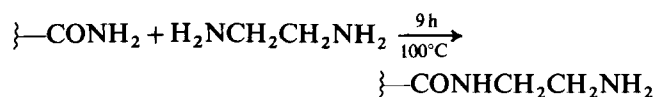
3.1 Synthesis of NNMBA-crosslinked polyacrylamides

Polyacrylamides with 2–20 mol% of NNMBA-crosslinks were obtained by the redox copolymerization of the monomers in water at 80°C using potassium persulphate as initiator. The polymerization reaction is depicted in Scheme 1. Polyacrylamides with varying extents of the crosslinks were prepared by adjusting the mol% of the monomers in the feed. With increasing crosslinking the rigidity of the polymer increased and hence the swelling in water also varied.

In NNMBA-crosslinked polyacrylamides, the networks are heterogeneous because of the mechanism of polymerization, which consists of three stages.¹⁹ The composition of the polymer in each stage is different and hence microdomains of different structure are formed.

3.2 Transamidation of crosslinked polyacrylamides: preparation of poly(N-2-aminoethylacrylamide)s

Amino functions were introduced into NNMBA-crosslinked polyacrylamides by transamidation with ethylenediamine at 100°C for 9 h. Ethylenediamine itself was used as the solvent. The reaction is represented in Scheme 2.



Scheme 2. Transamidation of NNMBA-crosslinked polyacrylamides with ethylenediamine.

The amino functions were detected by the semi-quantitative ninhydrin reaction and estimated by equilibrating definite amounts of the resin with known concentrations of excess hydrochloric acid, and by estimating the residual acid by titration with alkali. The amino capacity varied with the extent of crosslinking in the polymer matrix (Fig. 1).

With increase of the NNMBA-crosslinking the amino capacities increased up to 8% crosslinking and decreased

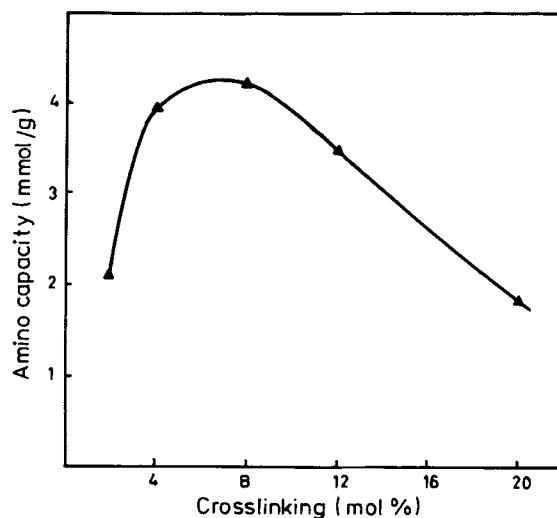
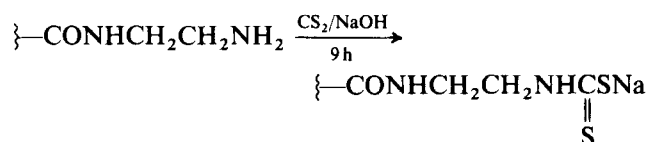


Fig. 1. Dependence of transamidation on the extent of NNMBA-crosslinking.

thereafter. Normally a higher amino capacity would be expected for the low crosslinked system because of the increased availability of the active sites for functionalization.²⁰ However, the amino capacity of the 2% crosslinked system is only 2.1 mmol g⁻¹. This may be explained on the basis of the heterogeneity developed in the crosslinked resins, or by the additional crosslinking arising from multi-transamidation with ethylenediamine. This latter possibility is supported by the low swelling of the 2% crosslinked resin. Polyacrylamides crosslinked with tetrafunctional crosslinking agents can have microdomains of varying characteristics, and when the gels are functionalized the resulting polymers have reactive sites in different microenvironments. Thus the 8% crosslinked resin may have microdomains more favourable for transamidation, which accounts for its higher amino capacity. In highly crosslinked systems the amide groups are buried within the crosslinks and are less accessible for transamidation.

3.3 Preparation of dithiocarbamate resin

Amino polyacrylamides with varying extents of NNMBA-crosslinks were converted to the corresponding dithiocarbamates by treatment with five-fold molar excess of carbon disulphide and alkali in aqueous medium. The dithiocarbamylation is depicted in Scheme 3.



Scheme 3. Dithiocarbamylation of NNMBA-crosslinked aminopolyacrylamides.

3.4 Complexation of dithiocarbamate resins: effect of the extent of crosslinking on complexation

The complexations of the dithiocarbamate functions supported on NNMBA-crosslinked polyacrylamides in different structural environments were investigated for Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) ions. For all the metal ions the metal ion intake increased with increasing crosslinking, showed a maximum at 8% crosslinking and decreased thereafter (Fig. 2). Similar observations were made in the case of NNMBA-crosslinked polyacrylamide-supported reagents.²¹

The NNMBA-crosslinks with their hydrophilic/hydrophobic balance and lower rigidity impart moderate swelling in water. This is important in the collection of metal ions from aqueous medium, as it favours the diffusion of metal ions into the swollen polymer matrix. The complexation was minimum for Co(II) and Ni(II) ions. Hg(II) has an entirely different range of complexation compared with the other metal ions (Table 1).

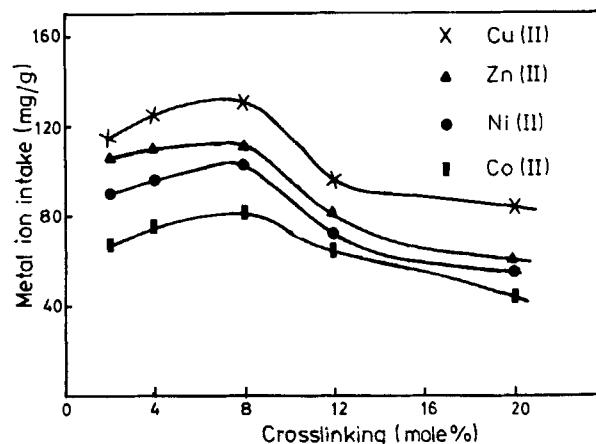


Fig. 2. Complexation of dithiocarbamates versus extent of NNMBA-crosslinking in the polyacrylamide-support.

The observed trend in complexation is Hg(II) >> Cu(II) > Zn(II) > Ni(II) > Co(II), which is in agreement with the reactivity of dithiocarbamate ligands towards various metal ions.²²

3.5 Time-course of complexation

The time-dependence of the complexation of Co(II), Ni(II), Cu(II) and Zn(II) ions was followed by noting the change in concentrations of the metal salt solutions at regular intervals of time. The 4% crosslinked resin was used for these investigations. The time profiles are given in Fig. 3. The complexations of Co(II) and Ni(II) were completed in 0.5 h, Cu(II) in 2 h and Zn(II) in 2.5 h. The hydrophilic and semi-rigid nature of the crosslinks has a significant role in the interaction of the ligands buried in the crosslinks with the metal ions in aqueous medium.

3.6 Recyclability of complexed resins

The recyclability of the dithiocarbamate resin was investigated in the case of the Cu(II)-complexed 4% NNMBA-crosslinked resin. The resin on treatment with 3N nitric acid desorbed the complexed Cu(II) quantitatively. The acid-treated resin was neutralized and again subjected to dithiocarbamylation. The complexation of

TABLE 1. Metal ion intakes of dithiocarbamate functions supported on NNMBA-crosslinked polyacrylamides

DVB (mol%)	Metal ion intake (mg g ⁻¹)				
	Co(II)	Ni(II)	Cu(II)	Zn(II)	Hg(II)
2	51	66	126	117	890
4	47	52	103	72	756
8	38	45	83	51	655
12	28	37	52	39	409
20	10	—	9	—	130

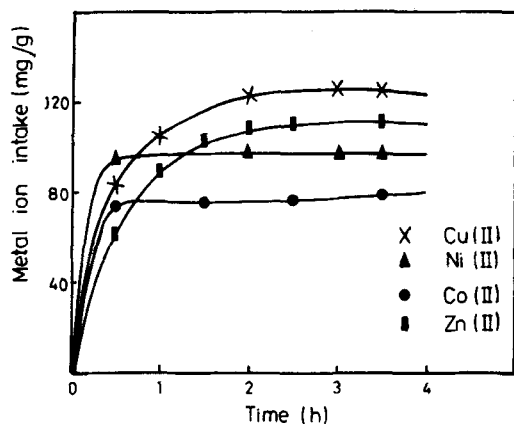


Fig. 3. Time-course of complexation.

the refunctionalized resin was not successful. A resin with initially $122 \text{ mg Cu(II) g}^{-1}$ of the resin after recycling complexed only 68 mg of the metal ion. This is because of the acid-catalysed decomposition of dithiocarbamate functions to protonated amine and carbon disulphide as reported in the case of low molecular weight dithiocarbamates.²³

3.7 Swelling studies

The equilibrium water contents (EWCs) of the various dithiocarbamate resins and their complexes with a definite amount of copper are given in Fig. 4. The EWCs of the uncomplexed dithiocarbamate resins were in the range 52–77%. This first increases with increasing crosslinking and then decreases because of the increased rigidity of the polymer matrix. The swelling of the 2% crosslinked resin is lower than expected. This arises from the multi-transamidation with ethylenediamine, resulting in the formation of a highly crosslinked system. The swellings of the complexed resins are lower than those of the uncomplexed resins. This reduction arises from crosslinking by complexation with metal ions, resulting in decreased intake of the solvent.²⁴ This reduction is higher

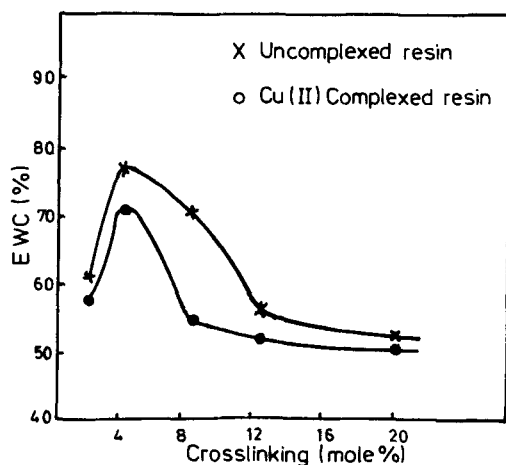


Fig. 4. EWCs versus extent of NNMBA-crosslinking in uncomplexed and complexed resins.

in the case of the 4, 8 and 12% crosslinked systems than for the 2 and 20% crosslinked systems, which have almost the same reduction in swelling after complexation. The much higher reduction in swelling after complexation of the 8% crosslinked resin is due to the contraction of voids in the polymer matrix by complexation. The co-operative contribution of the randomly distributed dithio functions for complexation makes the complexed polymer matrix more compact.

3.8 Infrared spectra

The IR spectra of the polyacrylamide-supported dithiocarbamates and their derived metal complexes showed absorption characteristics of amides, dithiocarbamates and metal-sulphur bonds. The C=O and N—H absorptions of the amide groups were observed at 1660 and 3400 cm^{-1} , respectively. The dithiocarbamates showed absorptions mainly in three regions: the peak in the region 1550 – 1450 cm^{-1} is associated with the thioureide vibration and is attributed to the C—N vibration of the CS_2 — NR_2 bond.²⁵ A second IR spectral region between 1050 and 950 cm^{-1} is associated with the (CSS) vibration. In the metal complexes this peak is broadened and showed a splitting of less than 20 cm^{-1} , indicating the bidentate coordination of the dithiocarbamates.²⁶ The IR spectral region between 400 and 200 cm^{-1} is associated with the M—S translational vibrations.²⁷ In the case of the Cu(II) complexes of the polymer ligands these peaks are seen in the regions 370 – 340 and 260 – 240 cm^{-1} . For the Ni(II) complexes the Ni(II)—S translational vibrations are seen in the region 390 – 380 cm^{-1} and at 340 and 240 cm^{-1} .

3.9 Thermogravimetric studies

The TG curves of the Cu(II) and Ni(II) complexes of dithiocarbamate functions supported on polyacrylamides with 4, 8, 12 and 20 mol% of NNMBA-crosslinks are given in Figs 5 and 6, respectively.

The TG curves of the Cu(II) complexes of 4 and 20 mol% of NNMBA-crosslinks showed three stages of

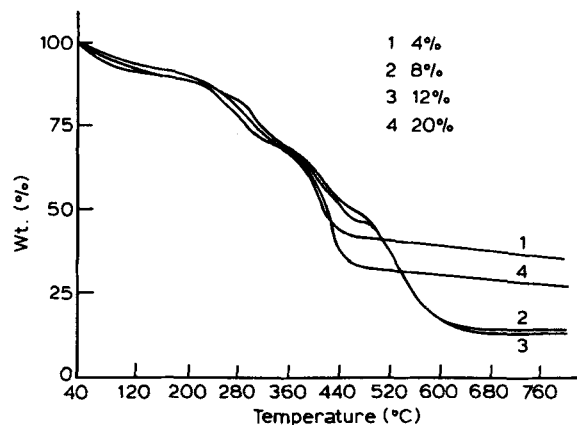


Fig. 5. TG curves of the Cu(II) complexes of dithiocarbamates with varying extents of NNMBA-crosslinks.

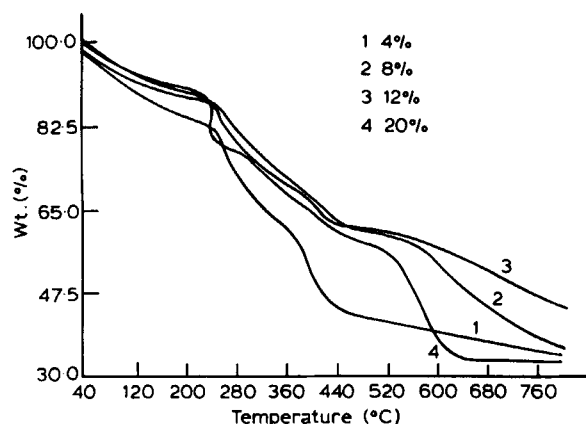


Fig. 6. TG curves of the Ni(II) complexes of dithiocarbamates with varying extents of NNMBA-crosslinks.

decomposition, whereas the 8 and 12% crosslinked systems had four stages. For the Ni(II) complexes, except the 4% crosslinked system, all had four stages. In all cases the first stage can be considered as the removal of adsorbed or co-ordinated water molecules present in the complexes. In Cu(II) and Ni(II) complexes this stage occurred over the temperature range 30–204°C, with mass losses between 8 and 12%. The second-stage decom-

TABLE 2. Phenomenological data of the thermal decomposition of the Cu(II) and Ni(II) complexes of NNMBA-crosslinked polyacrylamide-supported dithiocarbamates

NNMBA (mol%)	Decomposition temperature range in TG (°C)		Peak temperature in derivative thermogravimetry (°C)	Mass loss (%)
	T_i	T_f	T_s	
Cu(II) complexes				
4	347	497	410	26
8	377	471	424	16
12	375	477	383	18
20	361	478	431	27
Ni(II) complexes				
4	349	491	407	20
8	349	472	407	20
12	372	490	410	14
20	371	478	417	19

TABLE 3. Kinetic parameters of the thermal decomposition of Cu(II) complexes of polyacrylamide-supported dithiocarbamates with varying extent of NNMBA-crosslinks

NNMBA (mol%)	Equation (1)				Equation (2)			
	E (kJ mol ⁻¹)	A (s ⁻¹)	ΔS (J)	r	E (kJ mol ⁻¹)	A (s ⁻¹)	ΔS (J)	r
4	169.1	9.4×10^{10}	-41.7	0.9842	169.5	1.7×10^{11}	-36.9	0.9838
8	134.3	2.7×10^9	-187.5	0.9971	134.9	4.9×10^4	-182.5	0.9971
12	132.7	1.6×10^9	-190.6	0.9937	133.7	3.2×10^9	-184.9	0.9976
20	153.8	2.5×10^9	-72.1	0.9941	154.6	7.5×10^9	-63.0	0.9951

positions were in the temperature range 175–233°C for Cu(II) complexes and 175–377°C for Ni(II) complexes. This stage occurs in two steps. The mass losses corresponding to the second stage were in the range 12–25% and 12–44% for the Cu(II) and Ni(II) complexes, respectively. The two-step decomposition may be a function of the slow decomposition of unfunctionalized amide groups and free ligands in the complexes. The third stage in all the cases was used for kinetic analysis of decomposition. The phenomenological data of the Cu(II) and Ni(II) complexes are given in Table 2.

The differential (eqn (1))²⁸ and the approximation methods (eqn (2))²⁹ were applied for the mathematical analysis of the TG curves using the least-squares method. The kinetic data and the correlation coefficients are given in Tables 3 and 4:

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

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

The values for the activation energy vary with the extent of NNMBA-crosslinking. For the Cu(II) complexes the activation energy decreases with increasing crosslinking up to 12%. For the Ni(II) complexes the activation energy decreased with crosslinking up to 8%, increased at 12% crosslinking and decreased thereafter. The activation energy (E) and the extent of crosslinking (C) fit a cubic polynomial of the type

$$E = a + bC + cC^2 + dC^3$$

where a , b , c and d are numerical constants. The specific equation for the Cu(II) complex is

$$E = 261.9 - 32.0C + 2.4C^2 - 0.0552C^3$$

and for the Ni(II) complexes

$$E = 308.6 - 61.6C + 6.4C^2 - 0.1865C^3$$

The plots of activation energy (E) versus extent of crosslinking (C) for the two complexes are given in Fig. 7. In the case of Cu(II) complexes the minimum thermal stability is for the 10% crosslinked system within the chosen limits of the experiment. Similarly, the Ni(II) complexes have minimum thermal stability at 7%

TABLE 4. Kinetic parameters of the thermal decomposition of Ni(II) complexes of polyacrylamide-supported dithiocarbamates with varying extent of DVB-crosslinks

NNMBA (mol%)	Equation (1)				Equation (2)			
	<i>E</i> (kJ mol ⁻¹)	<i>A</i> (s ⁻¹)	ΔS (J)	<i>r</i>	<i>E</i> (kJ mol ⁻¹)	<i>A</i> (s ⁻¹)	ΔS (J)	<i>r</i>
4	154.9	7.2×10^6	-120.5	0.9979	154.2	1.0×10^7	-117.5	0.9982
8	138.0	3.5×10^5	-145.7	0.9995	138.5	6.4×10^5	-140.7	0.9995
12	179.6	4.5×10^6	-86.2	0.9900	180.0	8.1×10^6	-81.3	0.9901
20	170.7	9.3×10^7	-99.3	0.9942	170.9	9.7×10^7	-99.0	0.9942

crosslinking and maximum thermal stability at 16% crosslinking. The higher thermal stabilities of the metal complexes may arise from the additional stability gained by the formation of stable ring structures.³⁰ The bidentate co-ordination structure of the dithiocarbamate would favour ring complexes.²⁶

3.10 Scanning electron microscopy

The scanning electron micrographs of the uncomplexed and complexed resins are given in Fig. 8. The surface of the uncomplexed resin appeared smoother than that of the complexed resin. The rough appearance of the complexed resin is because of the rearrangement of the orderly arranged polyacrylamide chains by complexation with metal ions. This results in an increase in disorder of the system.

4 CONCLUSION

The foregoing investigations on the preparation of crosslinked polyacrylamides, their functionalization and complexation suggest that there is a definite correlation between the extent of functionalization and extent of crosslinking. The complexation behaviour of dithiocarbamates depends on their molecular character and the

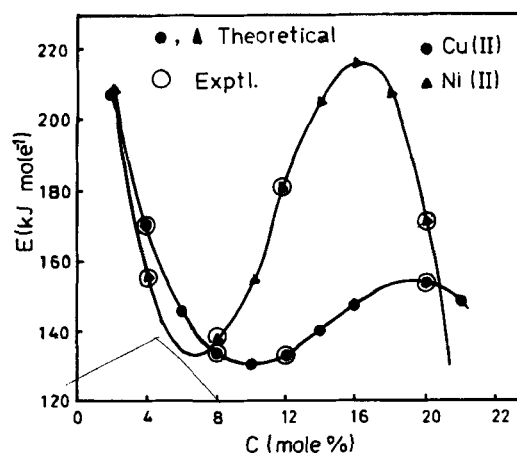
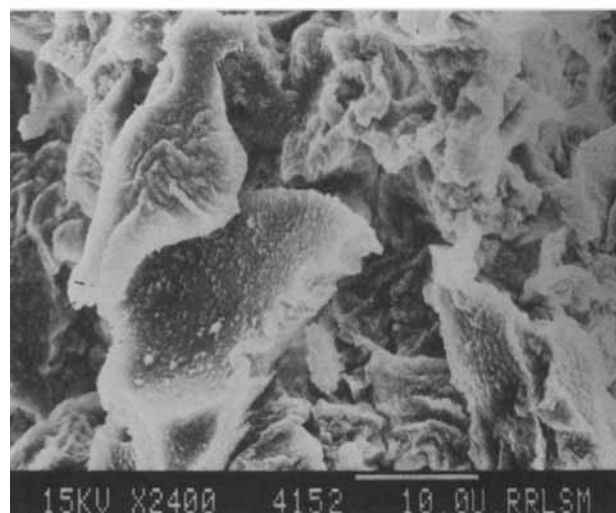


Fig. 7. Activation energy versus extent of NNMBA-crosslinking in the Cu(II) and Ni(II) complexes of dithiocarbamates with varying extents of NNMBA-crosslinks.

extent of crosslinking. The swelling of the crosslinked polymeric ligands in water depends on the extent of crosslinking. The swelling of the complexed resins was lowered by complexation. Recyclability of the complexed resins was not possible because of their decomposition in the presence of acids. The thermal stability increases on complexation and the thermal stability of the Ni(II)



(a)



(b)

Fig. 8. Scanning electron micrographs of (a) uncomplexed resin and (b) complexed resin.

complexes are higher than those of the Cu(II) complexes. Thermal stability of the complexes varies with the extent of crosslinking in the complex. In the case of Cu(II) complexes thermal stability decreases up to 12% crosslinking and increases thereafter. In the case of Ni(II) complexes thermal stability first decreases with NNMBBA content up to 7% crosslinking, then increases up to 16% crosslinking and decreases thereafter. The change in surface morphology on complexation is shown by the SEM patterns.

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