Polymer-Metal Complexes of N,N'-Methylene-bis-acrylamide(NNMBA)-Crosslinked Polyacrylamide-Supported Glycines: Effect of the Degree of Crosslinking On Metal ion Complexatlon and Concentration

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POLYMER-METAL COMPLEXES OF N,N'-METHYLENE-BIS-ACRYLAMIDE (NNMBA)-CROSSLINKED POLYACRYLAMIDE-SUPPORTED GLYCINES: EFFECT OF THE DEGREE OF CROSSLINKING ON METAL ION COMPLEXATION AND CONCENTRATION

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ABSTRACT

Glycine functions were incorporated into 2-20 mol% N,N'-methylene-bis-acrylamide (NNMBA)-crosslinked polyacrylamides by transamidation with excess sodium salt of glycine. Complexation characteristics of glycine functions in different structural environments were investigated towards Co(II), Ni(II), Cu(II) and Zn(II) ions. The observed trend in complexation was found to be: Cu(II) > Ni(II) > Co(II) > Zn(II). The polymeric ligands and metal complexes were characterized by various spectral techniques. The polymeric ligands could be recycled several times and the metal ion desorbed resins showed specificity to the desorbed metal ion than other metal ions. This originates from the development of certain 'pockets' left by the desorbed metal ion or the 'memory' of the polymeric ligands for the desorbed metal ion. This lightly crosslinked systems showed much faster rebinding kinetics. The conditions of metal ion binding and rebinding were optimized to exploit the specific and selective separation of metal ions using metal ion desorbed systems. The specificity and selectivity characteristics depend on the degree of NNMBA crosslinking.

INTRODUCTION

The metal complexation behavior of polymeric ligands has attracted much attention in areas of metal ion separation, catalysis and bioinorganic chemistry [1-3]. in a polymeric ligand or polymer-metal complex, the active center is only an infinitesimal part of the three-dimensional polymer-support. Hence, its complexing ability and physicochemical properties would be greatly influenced by the characteristics of the macromolecular matrix [4-6]. The chemical nature of the monomer, nature and degree of crosslinking, conditions of polymerization, porosity, surface area and spacer between the ligand function and the polymer-support are the major factors contributing to the topography of the polymer-support and thus complexing ability of supported ligands [7-8].

Usually in chelating polymers, metal ion separation is achieved by utilizing the differences in the stabilities of various metal complexes [9]. This could be achieved by varying the conditions of metal ion complexations. Later, metal ion specific polymers were designed by fixing the coordination sphere of the metal complexes by the prearrangement of the metal centers by template polymerization [10]. But this procedure requires a very high degree of crosslinking to maintain the coordination geometry sculpt during polymerization. The high degree of cross-linking ncessitates severe conditions for the desorption of the complexed metal ion and the rebinding kinetics was very slow [11]. Since the template polymerization method is based mainly on solution or bulk polymerization techniques, usually the resultant polymers are formed as bulk resins. This necessitates the grinding and sieving of the samples before use, which results in the partial destruction of the imprinted structures during grinding. In order to overcome these limitations, "surface template polymerization" has been reported by Takagi *et al.* [12].

In this paper, we report the synthesis, characterization and selective metal ion complexation of NNMBA-crosslinked (2-20 mol%) polyacrylamide-supported glycines. The specificity of metal ion desorbed systems for the desorbed metal ion, optimization of the conditions of metal ion binding and rebinding, kinetics and metal ion concentration using the metal ion desorbed systems are also described.

EXPERIMENTAL

All the reagents were of certified of ACS reagent grade. The IR spectra were recorded on a Shimadzu 470-spectrometer using KBr pellets. The UV-visible spectra were recorded on a Shimadzu UV-160 A spectrometer.

Preparation of NNMBA-Crosslinked Polyacrylamides with Glycine Functions

The preparation of polyacrylamides with 2-20 mol% of NNMBA cross-links are reported earlier [13]. Glycine functions were incorporated in to crosslinked polyacrylamides in different structural environments by transamidation with excess sodium salt of glycine at $100\,^{\circ}C$ for 24 hours. The functionalized polymers were collected by filteration, soxhleted using methanol and acetone, and dried in an oven at $80\,^{\circ}C$.

Estimation of Carboxyl Capacity

The carboxylate resin (100 mg) was equilibrated with HCl (0.2N, 10 mL) with stirring for 24 hours. 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.

Metal Ion Complexation

The crosslinked carboxylate resins (100 mg) was stirred with metal salt solution (0.05 N, 50 mL) for 24 hours. The complexed resins were collected by filtration and washed with excess distilled water to remove uncomplexed metal ions. The concentration of Co(II), Ni(II) and Cu(II) solutions were followed by UV-visible spectrometry and Zn(II) by complexometric method.

Desorption of Complexed Metal Ions

The complexed metal ions were desorbed using H_2SO_4 (0.2 N) and the acid treated resins were washed with distilled water to remove the unreacted HCl and neutralized using dilute NaOH (0.1 N).

Rebinding of Metal Ions

The neutralized metal ion desorbed resins were treated with the desorbed metal ion (0.05 N, 50 mL) and other metal ions and the extent complexation were followed by UV-visible spectrometry for Co(II), Ni(II) and Cu(II) ions and for Zn(II) ion complxometric titration aganist EDTA was used.

Kinetics of Metal Ion Complexation

Different sets of NNMBA-crosslinked polyacrylamide-supported glycines (50 mg) were added to copper sulfate solution (0.05 N, 50 mL) and shaken in a thermostat at different time intervals at $30\,^{\circ}C$ and $40\,^{\circ}C$. The metal ion complexation were followed by UV-visible spectrometry. The same was repeated for metal ion desorbed resins.

Effect of pH Dependence

Different sets of crosslinked carboxylate resins (100 mg) were added to metal salt solution at different pH. At 0.05 N concentration, the natural pH for different metal ions are: Co(II) = 5.1, Ni(II) = 5.8, Cu(II) = 5.1 and Zn(II) = 4.8. The flasks were equilibrated by placing in a thermostated shaker for 24 hours. The uncomplexed metal ions were washed using distilled water and analyzed using UV-visible spectrometry. The same experiment was repeated for metal ion desorbed resins.

Selectivity Studies

To each of the metal ion desorbed polyacrylamide-supported glycine ligands, a mixture of metal ions: $CuSO_4.5H_2O$ (50 mL) + $CoCl_2. 6H_2O$(50 mL); and $CuSO_4. 5H_2O$ (50 mL) + $NiSO_4 . 6H_2O$ (50 mL) and stirred for 24 hours. The amounts of different metal ions complexed were estimated using multi-component UV-visible spectrometry.

RESULTS AND DISCUSSION

Preparation of Polyacrylamide-Supported Glycines

NNMBA-crosslinked (2-20 mol%) polyacrylamides were prepared by free radical solution polymerization as reported earlier [13]. Glycine functions are incorporated into crosslinked polyacrylamide by transamidation with excess sodium salt of glycine as represented in Scheme 1.

The carboxyl capacity of the resulting polymers were determined by titration with alkali. The carboxyl capacity increases from 2-8 mol% and then decreases (Figure 1). Similar observations of increased reactivites of polyacrylamides with moderate NNMBA-crosslinks (8-10 mol%) are reported [14, 15]. This anomalous observation of reactivity arise from the heterogeneous distribution of the crosslinks which is inevitable in the polymerization of acrylamide with NNMBA [16]. After 8% crosslinking, the carboxyl capacity decreases with increasing crosslinking due to the reduced availability of the functional groups buried within the crosslinks.

Metal Ion Complexation of 2-20 mol% NNMBA-Crosslinked Polyacrylamide-Supported Glycines

The metal ion complexation of the glycine functions in different structural environments were investigated towards Co(II), Ni(II), Cu(II) and Zn(II) ions by

$$\text{-CONH}_2 \ + \ 2\text{HNCH}_2\text{COO}^- \text{ Na}^+ \quad \xrightarrow[\text{20 h}]{100^{\circ}\text{C}} \quad \text{-CONHCH}_2\text{COO}^- \text{ Na}^+$$

Scheme 1: Transamidation of NNMBA-crosslinked polyacrylamide with sodium salt of glycine
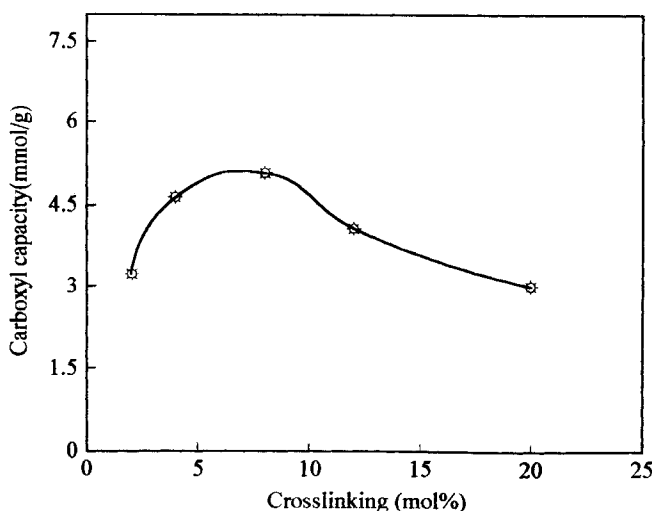

Figure 1: Dependence of carboxyl capacity on the degree of NNMBA crosslinking.

equlibration with (0.05 N) solution at its natural pH. The amount of metal ion complexed were estimated using UV-visible spectrometry. The observed trend in complexation was found to be: Cu(II) > Ni(II) > Co(II) > Zn(II). The degree of NNMBA crosslinking has a significant effect on the interaction of the supported ligands with metal ions. The complexation increases with the extent of crosslinking, passes through a maxium at 8% and then decreases (Figure 2). Generally, a higher metal ion intake would be expected for a low crosslinked system because of the increased availability of ligand functions [17]. But the heterogenity developed in the polymer matrix leads to low metal ion intake for low crosslinked systems. Similar variations in metal uptake with increasing NNMBA crosslinks are reported [18].

IR Spectra

NNMBA crosslinked polyacrylamide showed amide -NH and C=O at 3500 and 1658 cm^{-1}, respectively. The absorption of secondary amide groups in
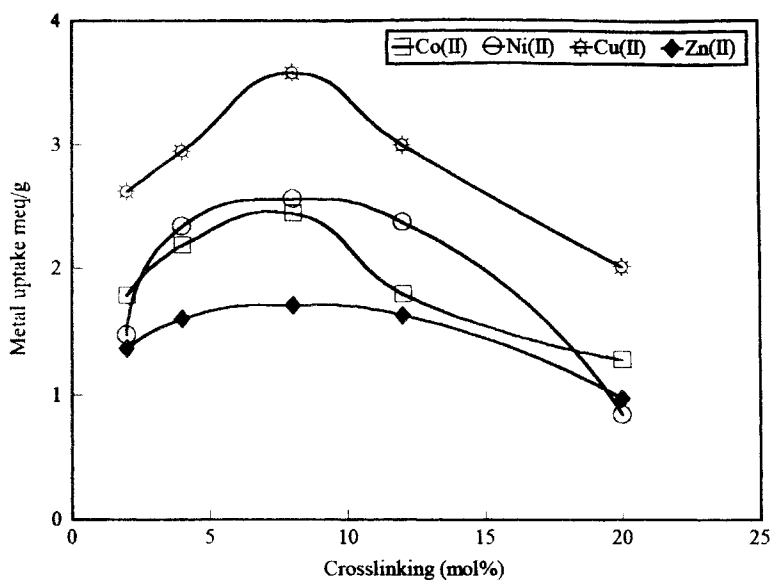
Figure 2: Effect of the degree of NNMBA crosslinking on metal ion complexation.

NNMBA crosslinking was observed at 1570-1500 cm^{-1}. In the functionalized polymer, the carboxylate group absorbs strongly at 1673 cm^{-1} and weakly at 1400 cm^{-1}. These bands originates from the asymmetric $(C\text{---}O)_2$ stretching. During complexation, the carboxylate group shifts to a lower frequency region i.e. from 1673 to 1640 cm^{-1} indicating its complexation with metal ion.

UV-Visible Spectra

        The structure and geometry of the resulting polymer metal complex is largely determined by the microenvironment of the polymer domain [19]. The polymer anchored Co(II) complex exhibits bands at 9500-11000 cm^{-1} and 18000-20500 cm^{-1} due to $^4T_{2g}(F)$- $^4T_{2g}$ (γ_1) and $^4T_{2g}$ (P) - $^4T_{2g}$ (γ_3) transitions in an octahedral geometry. In polymer anchored Ni(II) complexes, there are two spin allowed transitions $^3A_{2g}$ -$^3T_{2g}$ (P),10048-15543 cm^{-1} and $^3A_{2g}$ -$^3T_{2g}$ (P), 23624-24570 cm^{-1} gives near octahedral geometry. Due to Jahn-Teller distortions, the d^9 configuration of the Cu(II) ion complexed polymer, a distorted octahedral structure is obtained. xy-x^2-y^2 and xz, yz-x^2-y^2 transitions occur as the axial bond is lengthening and xy-x^2-y^2 transition shifts to blue region. In polymer anchored Zn(II) complex, the spectra obtained is ligand related and no d-d transitions occurs. Therefore, it would have a tetrahedral geometry.

Metal Ion Rebinding Studies of Metal Ion Desorbed Systems

In order to investigate the specific complexations of the metal ion desorbed resins, the complexed metal ions were desorbed using 2N H_2SO_4. The accessibility of the undisturbed, prearranged binding sites around the 'pockets' left by the desorbed metal ions towards the desorbed metal ion and other metal ions were evaluated by the metal ion rebinding studies of the neutralized acid treated ligands. On metal ion desorption, there developed certain 'cavities' or 'pockets' which is the coordination geometry of the desorbed metal ion and if these 'pockets' were not disturbed during the rebinding experimental conditions they would have an unusual memory for the desorbed metal ions resulting in its specific binding. The metal ion desorbed resins rebind, the desorbed metal ion quantitatively usually >97% of their original complexation (Table 1). The results of the specific binding of the desorbed metal ions are given in the marked column. This is also supported by the low binding of other metal ions by the desorbed resins. In the metal ion desorbed resins, the ligands are oriented in a specific direction which is suitable for the binding of the desorbed metal ions. Complexation of these specifically oriented ligands with other metal ions is less favored by the inaccessability of the unfavorable positions of these pre-oriented ligands. The polymeric ligands can be brought to its best conformation for the coordination sphere of a metal ion by adjusting the nature and degree of crosslinking. The specific binding of the desorbed metal ions increases with the increasing degree of crosslinking from 2-20 mol%. The 2 mol% crosslinked system has the low rebinding capacity compared to higher crosslinked systems. This points to the possibility of maintaining the stable geometry for the desorbed metal ion with increasing rigidity of the polymer-support. This also reduces the extent of deformation of the developed "cavities" during rebinding process.

Effect of pH Dependence on Metal Ion Complexation

The complexation of metal ions by a polymeric ligand is highly dependent on the equilibrium pH of the medium [20, 21]. The pH dependence of metal ion complexation was used for the selective separation of metal ions from a mixture of metal ions. Metal ion selectivity can be achieved by adjusting the pH of the medium. The interaction of 4 mol% NNMBA-crosslinked polyacrylamide-supported glycine ligands as a function of equilibrium pH was studied by batch techniques using Co(II), Ni(II), Cu(II) and Zn(II) ions. Since most of the metal ions are prone to precipitation at higher pH, investigations were limited to those pH values where precipitation was just prevented. Use of buffer solution for adjusting the pH would cause undesirable results due to the coordination of the ligand species with metal ions. Figure 3 represents the pH dependence on the metal ion complexation of the

TABLE 1. Metal Uptakes of Co(II)-, Ni(II)-, Cu(II)- and Zn(II)-desorbed 2-20 mol% NNMBA-crosslinked Polyacrylamide-supported Glycines.

| NNMBA (mol %)	Original metal uptake	Metal uptake by metal-desorbed resins(meq/g)[a]			
		Co(II)	Ni(II)	Cu(II)	Zn(II)
Co(II)-desorbed 2	1.79	1.08±0.02 (98.0%)	1.29±0.012 (87.6%)	1.07±0.010 (41.9%)	1.26±0.011 (91.8%)
4	2.19	2.15±0.015 (98.3%)	1.23±0.010 (52.3%)	1.30±0.013 (66.1%)	1.09±0.014 (68.1%)
8	2.45	2.45±0.014 (99.9%)	1.26±0.013 (73.3%)	1.55±0.017 (43.3%)	1.17±0.012 (64.4%)
12	1.81	1.80±0.015 (99.9%)	1.05±0.012 (43.9%)	0.95±0.014 (31.5%)	0.89±0.015 (54.6%)
20	1.30	1.27±0.013 (99.9%)	0.62±0.014 (73.6%)	0.60±0.011 (29.8%)	0.45±0.013 (46.7%)
Ni(II)-desorbed 2	1.48	1.75±0.015 (97.8%)	1.45±0.016 (98.3%)	2.51±0.010 (96.0%)	1.34±0.015 (97.7%)
4	2.34	1.50±0.013 (64.2%)	2.31±0.013 (98.3%)	2.00±0.014 (68.0%)	1.50±0.019 (93.5%)
8	2.56	1.50±0.014 (61.2%)	2.56±0.015 (99.7%)	1.50±0.016 (42.0%)	1.39±0.016 (81.0%)
12	2.39	1.02±0.011 (56.3%)	2.38± (99.7%)	1.50±0.017 (49.9%)	1.27±0.010 (77.8%)
20	0.84	1.02±0.017 (79.6%)	0.81±0.013 (96.7%)	1.30±0.012 (64.4%)	0.93±0.012 (96.5%)
Cu((II)-desobed 2	2.62	0.98±0.015 (55.1%)	1.27±0.016 (86.5%)	2.56±0.015 (97.6%)	1.35±0.011 (98.1%)
4	2.94	1.20±0.012 (55.0%)	1.50±0.017 (64.2%)	2.93±0.016 (99.7%)	1.21±0.017 (75.2%)
8	3.58	1.50±0.013 (60.1%)	0.69±0.015 (40.3%)	3.57±0.014 (98.8%)	1.33±0.016 (77.3%)
12	3.01	1.13±0.019 (62.5%)	0.69±0.019 (28.8%)	3.00±0.011 (99.8%)	1.07±0.014 (65.1%)
20	2.02	0.81±0.016 (63.3%)	0.51±0.014 (61.1%)	2.00±0.010 (99.3%)	0.77±0.013 (77.5%)
Zn(II)-desorbed 2	1.37	1.65±0.015 (92.2%)	1.61±0.016 (108%)	2.34±0.013 (90.6%)	1.32±0.016 (96.2%)
4	1.60	1.01±0.013 (46.0%)	1.61±0.016 (68.8%)	2.06±0.012 (88.6%)	1.60±0.018 (98.6%)
8	1.71	1.01±0.017 (41.2%)	2.09±0.018 (81.4%)	2.29±0.011 (61.6%)	1.71±0.013 (99.7%)
12	1.64	1.37±0.016 (76.0%)	1.85±0.014 (47.9%)	2.29±0.017 (76.0%)	1.63±0.016 (99.2%)
20	0.97	0.72±0.011 (56.2%)	0.86±0.012 (102%)	1.29±0.015 (63.8%)	0.96±0.011 (98.8%)

a: Average of three experiments
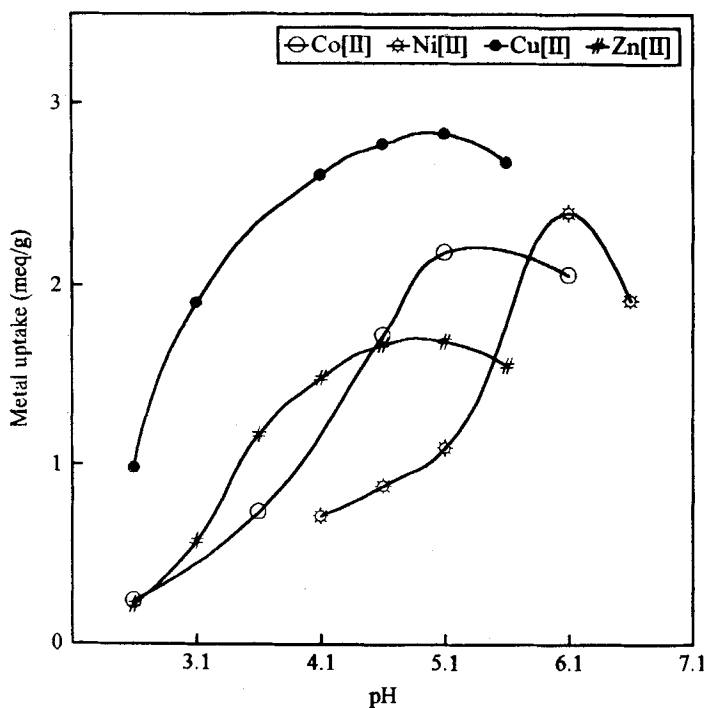
Figure 3: pH dependence on metal ion complexation of 4 mol% NNMBA-crosslinked polyacrylamide-supported glycine.

4 mol% NNMBA-crosslinked polymeric ligand at different pH. For all metal ions the complexation was found to be lower below its natural pH. But above the natural pH the complexation was found to be increased to a certain value and then decreased. The optimum pH for different metal ions was found to be: Co(II) = 5.4; Ni(II) = 6.2; Cu(II) = 5.4; and Zn(II) = 5.1.

The dependence of pH on the metal ion rebinding by the metal ion desorbed resin was also investigated. For this, Cu(II)-desorbed, 4 mol% NNMBA-cross-linked polyacrylamide-supported glycine was used. The results showed that with increasing pH there is no considerable increase in metal uptake as in the case of nacent complexation (Figure 4). For rebinding, the maximum pH was found to be at 5.4 instead of 51-5.4 in the case of original complexation. This suggests that for rebinding, the metal uptake is solely controlled by the 'preferential' geometry already present in the polymer matrix of the desorbed system. Also as in original complexation, there is no drastic change in Cu(II) uptake by the Cu(II)-desorbed resins. i.e. the pH has no significant effect on metal ion rebinding.
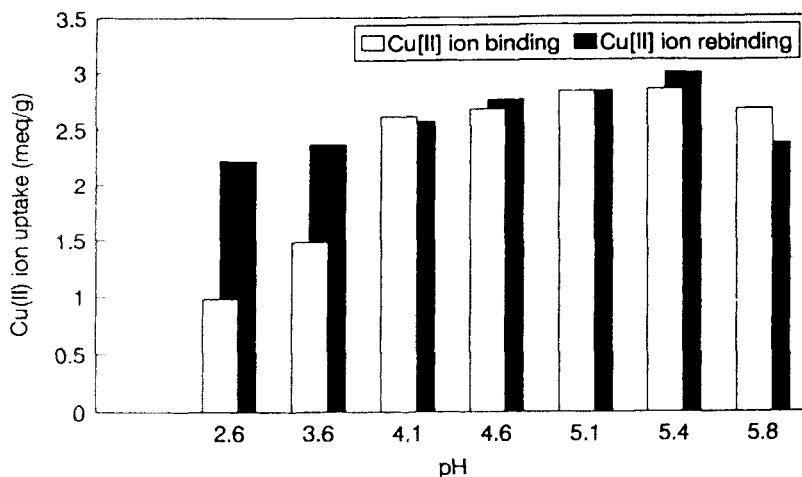
Figure 4: pH dependence on Cu(II) binding and rebinding of 4 mol% NNMBA-crosslinked polyacrylamide-supported glycine.
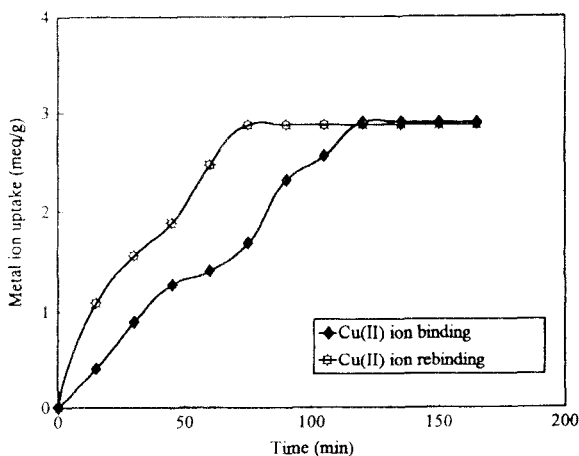

Figure 5: Time-course of Cu(II) ion binding and rebinding of 4 mol% NNMBA-crosslinked polyacrylamide-supported glycine.

Kinetics of Metal Ion Binding and Rebinding

The nature of polymer backbone and degree of crosslinking has a significant effect on the kinetics of metal ion complexation [22]. If the polymeric ligand is highly selective and has sufficient sorptive capacity but has poor kinetic property, its application for the concentration of metal ions may prove ineffective especially in the separation of metal ions [23].

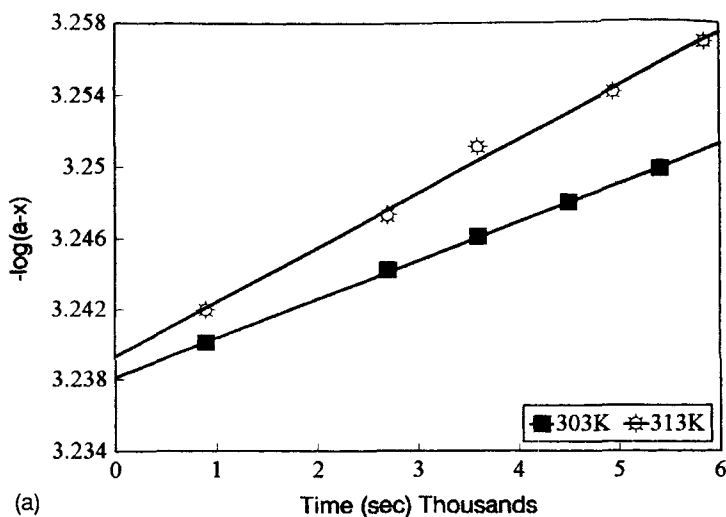**Figure 6 (a):** Kinetic plots for the metal ion binding of 4 mol% NNMBA-cross-linked polyacrylamide-supported glycine.
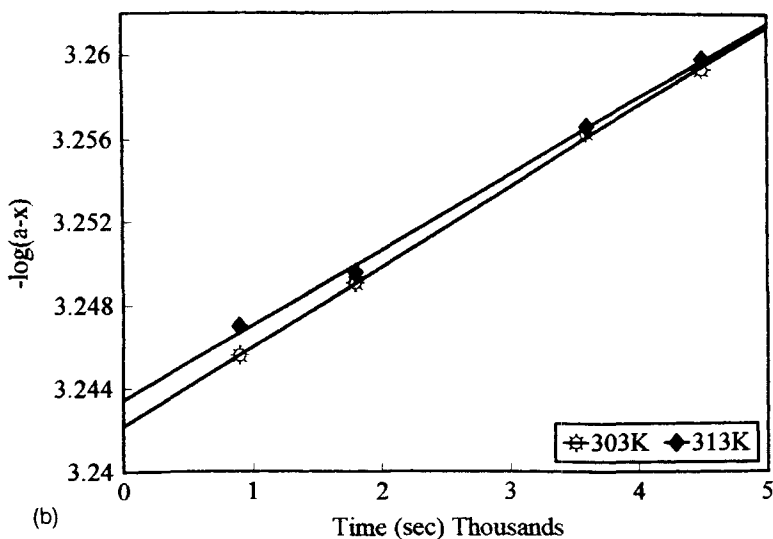
Figure 6 (b): Kinetic plots for the metal ion binding of 4 mol% Cu(II)-desorbed NNMBA-crosslinked polyacrylamide-supported glycine.

TABLE 2. Kinetic Parameters of Cu(II) Ion Binding and Rebinding of 4 mol% NNMBA-crosslinked Polyacrylamide-supported Glycine.

Complexation	ΔE (kJ/mol)	ΔS (J/mol)	A (s^{-1})
Cu(II)-binding	32.20	-206.24	1.722×10^2
Cu(II)-rebinding	3.31	-159.38	3.298×10^{-4}

In order to follow the time-course and kinetic parameters of metal ion binding and rebinding, the Cu(II) complexation of 4 mol% crosslinked resin and its Cu(II)-desorbed system were selected. Polymers with 200-400 mesh size were used for the study. The time required for the initial copper ion complexation was 2.5 hours. Whereas for rebinding, it requires only one hour with a $t_{1/2}$ of 0.5 hours (Figure 5). This indicates the favorable stable geometry kept by the desorbed metal ion resulting in its fast rebinding.

The results of the kinetic study are in agreement with first order kinetics as shown in Figures 6 a and b. The kinetic parameters calculated using the Arrhenius equation are given in Table 2. The high activation energy of the original polymeric ligand is required for the adjustment of the macromolecular chains from their normal positions for the required geometry for the complexed metal ions.

Metal Ion Selectivity Studies

In order to investigate the selectivity characteristics of (2-20 mol%) NNMBA-crosslinked polyacrylamide supported glycine ligands and metal ion desorbed systems, competitive rebinding experiments were carried out with pairs of metal ions at its natural pH. The results of the selectivity studies of the various crosslinked systems and their metal ion desorbed systems are given in Table 3. For the original polymer i.e. polymer without metal ion desorption, no selectivity was observed as evidenced from their low selectivity coefficient values. The size of the metal ion and the difference in the coordination geometry of the different polymer metal complexes are decisive in dictating selectivity. The metal ion desorbed system keeps in mind the coordination geometry of the desorbed metal ion. If this geom-etry is not disturbed during the rebinding experimental conditions, the metal ion desorbed systems, specifically and selectively bind the desorbed metal ions than other metal ions as depicted in Figure 7. But the metal ion desorbed systems showed selectivity towards the desorbed metal ions. Interestingly, the Cu(II)-

TABLE 3. Summary of Selectivity Studies 2-20 mol% NNMBA-Crosslinked Polyacrylamide SuppB. Maorted-Glycine (Original and Metal Ion Desorbed Systems).

| NNMBA (mol%)	Original metal ion	Rebinding pair of metal ions	Metal ion complexation of desorbed system from the mixture	Original complexation (meq/g)
2	Co(II)	Co(II)+Cu(II)	Co(II)=0.34, Cu(II)=1.51	1.78
	Ni(II)	Cu(II)+Ni(II)	Cu(II)=1.59, Ni(II)=1.49	1.47
	Cu(II)	Cu(II)+Co(II)	Co(II)=0.16, Cu(II)=2.54	2.62
	Cu(II)	Cu(II)+Ni(II)	Cu(II)=1.61, Ni(II)=1.14	2.62
Original polymer	Nil	Cu(II)+Co(II)	Co(II)=0.81, Cu(II)=1.76	
	Nil	Cu(II)+Ni(II)	Cu(II)=1.37, Ni(II)=1.30	
4	Co(II)	Co(II)+Cu(II)	Co(II)=1.78, Cu(II)=1.19	2.19
	Ni(II)	Cu(II)+Ni(II)	Cu(II)=1.069, Ni(II)=1.42	2.34
	Cu(II)	Cu(II)+Co(II)	Co(II)=0.00, Cu(II)=2.83	2.94
	Cu(II)	Cu(II)+Ni(II)	Cu(II)=1.89, Ni(II)=1.03	2.94
Original polymer	Nil	Cu(II)+Co(II)	Co(II)=0.89, Cu(II)=2.07	
	Nil	Cu(II)+Ni(II)	Cu(II)=1.51, Ni(II)=1.46	
8	Co(II)	Co(II)+Cu(II)	Co(II)=2.15, Cu(II)=1.43	2.45
	Ni(II)	Cu(II)+Ni(II)	Cu(II)=1.31, Ni(II)=1.71	2.56
	Cu(II)	Cu(II)+Co(II)	Co(II)=0.50, Cu(II)=3.49	3.57
	Cu(II)	Cu(II)+Ni(II)	Cu(II)=1.81, Ni(II)=1.63	3.57
Original polymer	Nil	Cu(II)+Co(II)	Co(II)=1.51, Cu(II)=1.95	
	Nil	Cu(II)+Ni(II)	Cu(II)=1.84, Ni(II)=1.57	
12	Co(II)	Co(II)+Cu(II)	Co(II)=1.51, Cu(II)=0.88	1.81
	Ni(II)	Cu(II)+Ni(II)	Cu(II)=1.31, Ni(II)=1.71	2.38
	Cu(II)	Cu(II)+Co(II)	Co(II)=.0004, Cu(II)=2.97	3.01
	Cu(II)	Cu(II)+Ni(II)	Cu(II)=1.55, Ni(II)=1.63	3.01
Original polymer	Nil	Cu(II)+Co(II)	Co(II)=0.55, Cu(II)=1.42	
	Nil	Cu(II)+Ni(II)	Cu(II)=1.66, Ni(II)=1.40	
20	Co(II)	Co(II)+Cu(II)	Co(II)=1.11, Cu(II)=0.56	21.28
	Ni(II)	Cu(II)+Ni(II)	Cu(II)=1.04, Ni(II)=0.49	0.84
	Cu(II)	Cu(II)+Co(II)	Co(II)=.0004, Cu(II)=1.91	2.02
	Cu(II)	Cu(II)+Ni(II)	Cu(II)=1.06, Ni(II)=0.49	2.02
Original polymer	Nil	Cu(II)+Co(II)	Co(II)=0.63, Cu(II)=1.31	
	Nil	Cu(II)+Ni(II)	Cu(II)=1.32, Ni(II)=0.72	
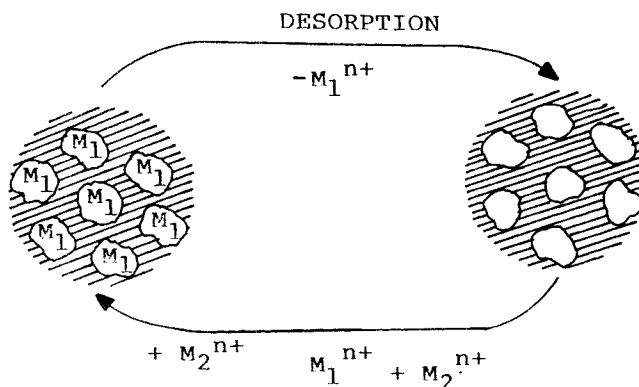
Figure 7:   Selective metal ion rebinding by the metal ion desorbed resins from a mixture of metal ions.

desorbed, 4 mol% NNMBA-crosslinked system specifically binds Cu(II) from a mixture of Cu(II) and Co(II) ions. Figure 8 shows a comparison of the selectivity characteristics of Cu(II)-desorbed, Co(II)-desorbed and non-complexed (original polymeric ligand) resins towards a Cu(II)-Co(II) mixture. The Co(II)-desorbed system and the original polymer binds two metal ions without any selectivity. But the copper ion desorbed systems selectively bind Cu(II) ions from a mixture of Cu(II) and Co(II) ions. With other pairs of metal ions, even though selectivity for the desorbed metal ions was observed a complete separation was not possible. The selectivity characteristics increased with increasing degree of crosslinking.

CONCLUSION

The preceding investigations of the metal complexation behavior of 2-20 mol% NNMBA-crosslinked polyacrylamide-supported glycine ligands revealed that the degree of NNMBA crosslinking has a significant effect on the extent of complexing ability of the supported carboxylate groups. The metal complexation increased with increasing crosslinking till 8% crosslinking and decreased further. The observed trend in complexation was: $Cu(II) > Ni(II) > Co(II) > Zn(II)$. The polymeric ligands and the metal complexes were characterized by their typical IR absorptions and UV spectra. The kinetics of metal ion complexation was found to be first order. The activation energy required for rebinding is much less compared to initial complexation. The nacent complexation depends on the pH of complex-
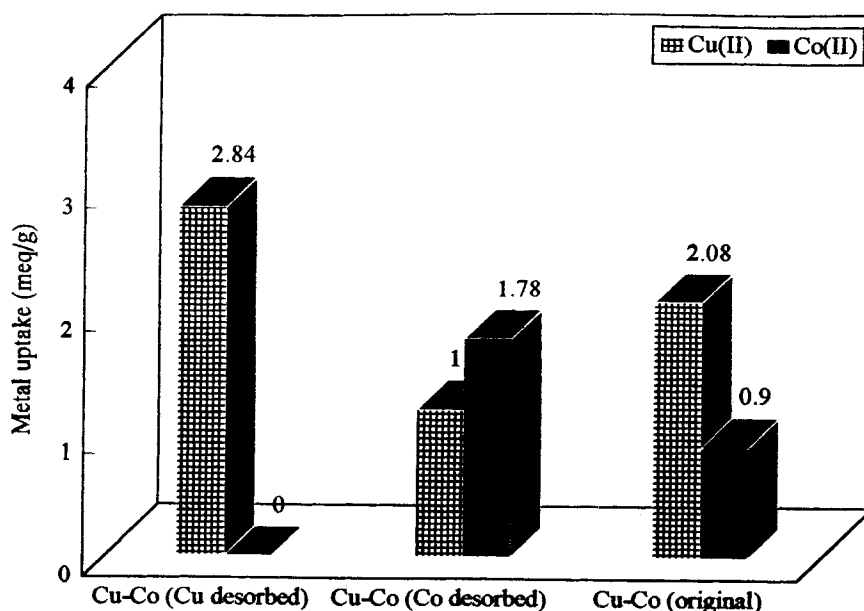
Figure 8: Metal ion selectivity studies of 4 mol% NNMBA-crosslinked poly-acrylamide-supported glycine using Cu(II)-Co(II) mixtures.

ation. But pH has no significant effect on the rebinding of metal ions. The metal ion desorbed systems showed specificity and selectivity towards the desorbed metal ions. Complete separation of Cu(II) ions could be achieved with Cu(II)-desorbed 4% crosslinked system from a mixture of Copper and cobalt ions.

ACKNOWLEDGEMENT

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