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Extraction of Copper by Selective Ion Exchangers with Pendent Ethyleneimine Groups—Investigation of Active States

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Abstract

Selective ion exchangers with pendent ethyleneimine groups of the type $-(NHC_2H_4)_n \cdot NH_2$, where n = 1 to 5, have been prepared, and their ability to extract cationic and anionic-chelated copper(II) ions has been evaluated. Copper has been extracted from aqueous solution, and the equilibrium capacities of extraction vary according to the active sites in the selective ion exchangers. The poor exchange properties of selective ion exchangers with short pendent groups have been related to the nature of the active coordination sites. The active sites on these selective ion exchangers change from two nitrogen atoms and two oxygen atoms (N_2O_2) with short chains (n = 1) to four nitrogens when n = 2 to 5. Those which have N_4 active sites appear to extract cationic copper(II) efficiently, but those with N_2O_2 sites have low capacities and copper is easily leached from the resin even when the loading of the resin is low. When copper is complexed to EDTA to form an anionic complex, a side chain like pentaethylene hexamine is required to extract the copper from aqueous solution. A macroporous polystyrene resin had a lower capacity for anionic chelated copper than a polystyrene gel resin with the same functional groups due to the poorer accessibility of the active (N_4) sites to the large anion.

INTRODUCTION

In previous studies we showed that copolymers with covalently bound pendent groups are able to extract copper and platinum group metals from aqueous solution (*1*). We also showed how it is possible to identify the active sites on copolymers which contain sulfur, nitrogen, and oxygen donor atoms. The term selective ion exchangers (SIE) is applied to those copolymers in which the bonding of the polymer to the metal ion has some degree of covalent character. The chemistry and the use of these exchangers has been reviewed (*2*), and their application to the extraction of base and precious metals has been outlined (*3*). With respect to copper, it is well known (*4*) that copper(II) has a high affinity for amine groups. However, it has been found that many SIEs with pendent amine groups are unable to extract copper(II) from solutions which contain soluble chelates (*5*) such as ethylenediamine tetraacetic acid (EDTA). Conversely, it has been shown (*6*) that some SIEs with pendent ethyleneimine groups are able to extract copper(II) ions from such solutions but the factors which govern the equilibrium capacities have not been determined.

In uncrosslinked copolymers (*7*) with donor nitrogen atoms, the entropic changes associated with the loss of coordinated water which accompanies the binding of the polymeric ligand to the metal favors the extraction of the metal by the polymer. Unfortunately, the uncrosslinked copolymers are soluble in water and, therefore, separation of the loaded soluble polymer is difficult. Pendent ethyleneimine ligands may, however, be covalently bound to insoluble polymer matrices such as poly(styrene) or polyacrylics (*8–11*). The factors which govern whether there will be extraction of cationic or anionic copper by copolymers or whether copper will remain complexed by EDTA in solution have not yet been satisfactorily determined. However, by analogy to the flexible uncrosslinked copolymer, it was considered that one of the variables is the length of the pendent chain and the number of nitrogen atoms in that chain.

When EDTA and copper(II) ions are present in solution, anionic species of the form $[CuEDTA]^{x-}$ are formed. The equilibrium by which copper is extracted from solution may br represented by the following Eq. (1) which holds for pH 7–11.

$$\underline{-(NH-C_2H_4)_nNH_2} + (Cu\text{-}EDTA)^{2-}) + EDTA^{2-} = \underline{-[(NH-C_2H_4)_nNH_2-Cu]^{2+} \cdot EDTA^{2-}} + EDTA^{2-} \quad (1)$$

The underlined part denotes the resin phase.

$$\underline{-[(NH-C_2H_4)_nNH_2-Cu]^{2+}\cdot EDTA^{2-}} + SO_4^{2-} + Mg^{2+} = \underline{-[NH-C_2H_4)_nNH_2-Cu]^{2+}\cdot SO_4^{2-}} + EDTA^{2-} + Mg^{2+} \quad (2)$$

In order to maintainn the electroneutrality within the ion exchanger, the anion, such as that of EDTA, balances the positive charge from the copper(II) ion. The EDTA anion may be removed from the ion exchanger by passing a solution (0.5 *M*) of magnesium sulfate through a column of the loaded ion exchanger. There is a competition for copper between the pendent chelating group on the copolymer and the EDTA in solution. However, when there is an excess of magnesium in solution, the EDTA is effectively eluted from the copper-loaded copolymer according to Eq. (2).

EXPERIMENTAL

The acrylic selective ion exchangers were prepared and supplied by Schwachula (*12*). Each of the acrylic-based copolymers had the same matrix polymer so that comparisons of the properties of the side chain could be made. The polystyrene samples were prepared using the procedure described by Egawa (*10, 11*) by using polystyrene which was crosslinked by 2% DVB. The capacity for copper was measured by the dynamic infinite volume solution technique. The molar ratio of EDTA to copper(II) in the feed solution was 2:1 with the concentration of copper(II) 1 mmol/dm^3. The total capacity for copper in the absence of EDTA was measured using an ammoniacal solution of copper(II) (1 mmol/dm^3).

Electron spin resonance spectra were measured on a Varian E-3 spectrometer by using resin samples loaded by copper(II) sulfate solution to a small percentage (5%) of the total capacity. Standard low temperature equipment (liquid nitrogen) was used throughout, and diphenylpicrylhydrazyl was used as an external calibrant.

RESULTS AND DISCUSSION

The copolymers may be formulated as [polymer]$-(NHC_2H_4)_nNH_2$ where n varies from 1 to 5. The first five copolymers in Table 1 have an ac-

TABLE 1
The Sorption Properties of the Copolymers[a]

Sorbent	Total anion exchange capacity (mmol HCl/cm^3)	Capacity (mmol Cu/cm^3)	
		Cu^{2+}_{aq}	Anionic Cu
	Acrylic Matrix		
EDA	1.04	0.24	0.11
DETA	2.91	0.51	0.145
TETA	3.06	0.56	0.18
TEPA	3.20	0.62	0.27
PEHA	3.47	0.73	0.41
	Styrene Matrix		
TETA (gelular)	2.95	0.59	0.29
TETA (macroporous)	2.32	0.52	0.055

[a]The notation refers to the side chain in copolymers of the type polymer–$(NH \cdot CH_2CH_2)_nNH_2$ for EDA (n = 1). EDA = ethylenediamine; DETA = diethylenetriamine (n = 2); TETA = triethylenetetramine (n = 3); TEPA = tetraethylenepentamine (n = 4); PEHA = pentaethylenehexamine (n = 5).

rylic backbone with the designated ligating groups covalently attached to the polymer. The total capacity of the copolymers for both anionic-chelated and free copper increase as the length of the side chain increases. It is noticeable that the capacity for both anionic and cationic copper is particularly low with the shortest group (n = 1) and the reasons for this may be interpreted from the electron spin resonance (ESR) spectra. With respect to EDA, that is, where n = 1, the acrylic-based ion exchanger has a low total ion-exchange capacity determined by hydrochloric acid adsorption of 1.04 mmol/cm^3. The measured capacity for copper(II) is 0.24 mmol/cm^3 in the absence of EDTA and 0.11 mmol/cm^3 in the presence of an excess of EDTA. Consequently, the measured capacity in the presence of EDTA is 22% of the maximum theoretical capacity for free copper(II), assuming that two nitrogen atoms are bonded to each copper. Clearly, a large proportion (78%) of the available nitrogen donor atoms may not be in use. However, if the coordination involves four nitrogen atoms per copper, then a greater proportion of the atoms may be involved in immobilizing the metal.

DETERMINATION OF THE ACTIVE SITES

The term "active site" is taken to mean the number and type of donor atoms coordinately bonded to the metal ion. The electron spin resonance data are given in Table 2 and in Fig. 1. A proportion of fine structure can be seen for each sample. The first point of note is that the ESR spectra give clear single signals with developed fine structure. There is no apparent contamination from aquo-copper ions, and we are dealing with well-defined specific sites involving N,O donor atoms. In additon, in no case were M = +1, +2 transitions observed nor was there any evidence of half-filled lines (*13*) which would imply metal-metal interaction. The ESR spectra are caused by "monomeric"-type species. The criterion for normal ESR in which *g*-parallel ($g_{\parallel}$) is greater than *g*-perpendicular (>2.02) is fulfilled when *g*-perpendicular is measured at one-third of the peak height. Consequently, for the majority of the samples we can exclude geometries giving a d_Z^2 ground state (i.e., trigonal bipyramidal, compressed octahedral, or *cis*-octahedral) (*13*). The presence of low $A_{\parallel}$ parameters sug-

TABLE 2
The Electron Spin Parameters of Copolymers with Pendent Ethyleneimine Groups

Acrylic matrix	$A_{\parallel}$ 10^4 cm^{-1}	$g_{\parallel}$ (G)	*g*-perpendicular (1/3) (G)	*g*-perpendicular (max) (G)	Active site
EDA (short)[a]	175	2.16	2.04	1.99	Uncertain
EDA (long)[b]	170	2.26	2.06	2.01(6)	N_2O_2
DETA	175	2.20	2.11	2.02	N_4
TETA	173	2.21	2.09	2.00	N_4
TEPA	173	2.20	2.11	2.03	N_4
PEHA	170	2.20	2.05	2.01	N_4
Polystyrene matrix					
gel DETA	210	2.17	2.07	1.99	Uncertain
gel TETA	175	2.21	2.09	2.02	N_4
macro DETA	183	2.14	2 peaks	1.97	N_4?
macro TETA	170	2.20	2.07	1.99	N_4
macro TEPA	173	2.21	2.07	2.01	N_4

[a]Equilibration of 5 min followed by rapid drying.

[b]Six hours equilibration.

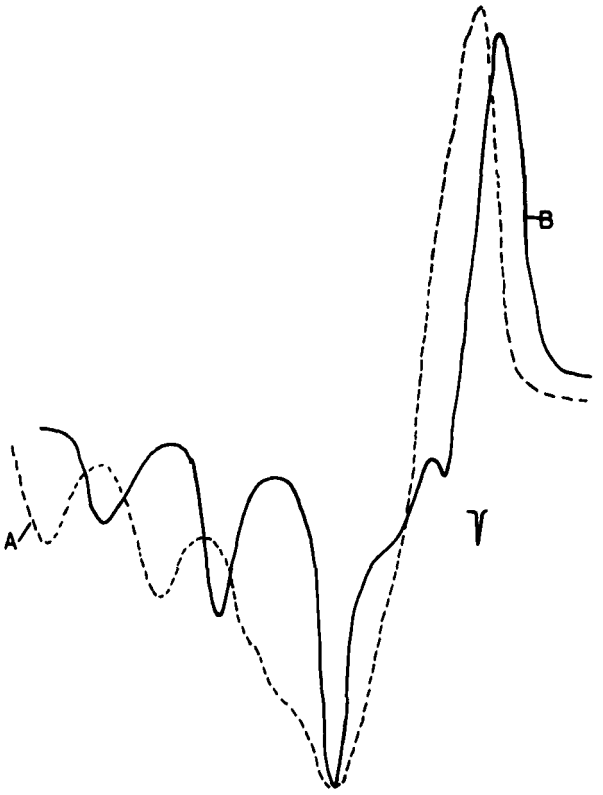

FIG. 1. Typical X-band spectra of the copper–copolymer complexes. A = copolymer with the ethylenediamine side chain (n = 1) with a long equilibration time of 6 h. B = copper–PEHA (n = 5).

gests that for most species a pseudotetrahedral geometry is involved. It has been known for some time that very low $A_{\parallel}$ values are diagnostic of this geometry, and there have been many attempts to correlate dihedral distortions in an originally square planar copper(II) moiety with $A_{\parallel}$ (*14*). Following the interpolations of Yokoi and Anderson (*15*) from $A_{\parallel}$ versus $g_{\parallel}$ plots for varying donor ligands, the parameter obtained are in accordance with particular active sites.

Ethylenediamine Side Chain

With respect to the copolymer with the ethylenediamine side chain (EDA) for which $n = 1$, there were two separate samples with quite different spectra. The first one, EDA (short) in Table 2, was equilibrated with copper sulfate for a short time (5 min) and then dried rapidly to prevent diffusion of the copper. The active site operation here is uncertain and does not clearly conform to a well-identified active site. This lack of a clear active site is probably related to the poor ion-exchange properties of this copolymer. It is interesting that the same polymer when equilibrated with copper ions for a longer time (6 h) has a different spectrum which is clearly related to an N_2O_2 active site (EDA long in Table 2). It is clear from the ESR spectra that the stereochemistries of the copper ion in the EDA complexes are different from all of the other acrylics with pendent amine groups. These differences arise because the chain is short and is unable to adopt the stereochemistry demanded by the copper ion. The importance of the length of the side chain is connected with the need for spacer groups with pendent chelating groups. Tsuchida (16), for example, has noted that pyridine groups with a spacer are more effective at removing copper from aqueous solution than when a spacer group is absent. A long spacer group allows the donor ligand atoms to achieve the required stereochemistry.

Other Acrylic Copolymers

There is a difference in the properties of EDA and PEHA for which the value of n is 5. For example, the exchange capacities of 0.73 and 0.41 for free and complexed copper(II), respectively. It appears that there is a higher percentage utilization of the active sites than is the case with the EDA polymer. One reason for the differences between the two resins could be that the active sites are different. The electron spin resonance spectrum for copper on PEHA is given in Fig. 1. It can be seen at a glance that the spectrum is quite different from those of copper on EDA. Moreover, the $A_{\parallel}$ and $g_{\parallel}$ values (*15*) are characteristic for N_4 coordination. It is possible that the nitrogen atoms all come from the same pendent chain but more likely that they come from two or more chains.

With respect to the copper-loaded DETA, TETA, and TEPA copolymers, the electron spin resonance spectra are also characteristic of the N_4 chromophore. The exchange capacities increase for both anionic and cationic copper as the length of the side chain increases. However, it is necessary that the nitrogen atoms come from different side chains because there are insufficient nitrogen atoms in the one chain.

The ability of the side chains to coordinate to copper increases with the length of the side chain as the successful extraction of copper depends on the formation of four copper to nitrogen bonds.

It has been shown (*17*) that amination using EDA produces a smaller degree of secondary crosslinking than is the case with all of the other amines. The copolymers DETA, TETA, TEPA, and PEHA are thought to have approximately the same degree of secondary crosslinking (*10, 16*). It appears that the increase of crosslinking from EDA to DETA, which would lead to a reduction in the capacity, is outweighed by the improvement of the properties by the increase in the chain length. The ability of the copolymer to use effectively the available nitrogen atoms seems to increase with the chain length. With the EDA copolymer, for example, the effective use amounts to 52% of the total nitrogens for an N_2O_2 active site. However, for the PEHA copolymer there appears to be a higher proportion of nitrogen atoms for coordination. Thus for the PEHA copolymer the effective use is $(0.73 \times 4/3.42)100 = 85\%$ so that the majority of the nitrogens are available for coordination—except for those which are adjacent to the polymer chain.

MATRIX EFFECTS

The capacity of a resin is clearly related to the accessibility of the active sites. In the case of uncomplexed copper cation, the Cu^{2+} aquo ion diffuses to the active site. However, when copper is complexed to EDTA the much larger anionic species have to diffuse. There is a remarkable difference in capacity between the styrene gel resin and the crosslinked styrene macroporous resin which both had 2% DVB. For the gel (TETA) and the macroporous resin (TETA), the functional groups are the same and the electron spin resonance spectra indicate that for both there is N_4 coordination. The capacity for the uncomplexed copper(II) ions is approximately the same for both resins (0.55 mmol/cm^3). However, the capacity for the copper in the anionic form is much lower in the styrene macroporous resin than with the styrene gel resin. This observation may be interpreted by the lack of accessibility of the active sites in the mac-

roporous resin to large anionic complexes and to the greater hydrophobic nature of the polystyrene copolymers. The polystyrene copolymers with short chains (n = 1 and 2) failed to give electron spin resonance spectra which could be clearly related to an identifiable site. However, the TETA copolymers gave spectra characteristic of the N_4 active site.

CONCLUSION

From the previous discussion it can be seen that for a given matrix the lengths of the pendent groups are important factors which determine whether there is coordination by four or fewer nitrogen atoms. Indeed, it can be inferred that the length of the side chain is one of the most critical factors with respect to the ability of selective ion exchangers to extract both cationic and anionic copper. An active site of the N_4 type seems to be crucial for effective extraction.

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