Preparation and Properties of a New Chelating Resin Containing Sulfur and Nitrogen Donor Atoms

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A novel chelating resin was obtained by incorporating 2-mercaptoethylamine into polystyrene divinylbenzene copolymer. Conversion of functional groups of the resin was confirmed by IR spectra, elemental analysis, hydrogen capacity, and protonation constants. The functionality of the resin is 0.45 mmol g⁻¹. The water regain as a function of pH was determined. The coordination behavior of the resin was investigated by IR, EPR and potentiometry. Effects of pH on adsorption of metal ions to the resin, both at large excess and limited amount of metal ions were examined. The resin exhibits exceptionally high affinity for soft metal ions, even in highly acidic aqueous media. EPR measurements at different copper loading were made. The results showed that the copper(II)-resin complex might be distorted tetragonal. Protonation constants and stability constants of the resin were determined at 25 °C and ionic strength of 0.5 M KCl solution. The selectivity of the resin toward metal ions decreased in the order: Au(III) > Pt(IV) > Ag(I) > Pd(II) > Hg(II) > Fe(III) > Cu(II) > Zn(II) > Cd(II) > Ni(II) $\equiv$ Co(II). Metal ion coordination occurs primarily at the nitrogen and sulfur donor atoms, but the polymeric backbone also makes significant contribution to metal binding. The resin demonstrated high promise for the collection and analysis of noble metal ions, especially from complex matrix samples.

INTRODUCTION

Despite advances in instrumentation and microcomputer technology, the determination of trace elements in complex matrices remains one of the most challenging areas of analytical chemistry. Chelation ion chromatography is considered as a very powerful technique for trace and ultra trace ion analyses in complex matrices.¹⁻¹³ The benefit of coupling chelation and ion chromatography provides a technique that makes possible the determination of trace elements in complex matrices often difficult or impossible to analyze by ion chromatography. In this respect, chelating resins or chelating-dye impregnated resins are usually employed as a concentrator or a separator. To improve the efficiency of chelation ion chromatography, it is important to develop new chelating resins of greater selectivity. However, the selectivity of a chelating resin is attributed mainly to the nature of the immobilized ligand on the base matrix.

By choosing an appropriate sorbent with the specific chelating groups and the optimum sorption conditions, one can obtain the required selectivity with respect to a certain element or a group of elements. Sulfur, a member of the third period having low-lying empty 3d orbitals, exhibits

markedly different bonding properties compared to nitrogen and oxygen. Although extensive studies on metal complexes of bi- and tridentate sulfur-nitrogen chelating agents have been reported in the literature, tetra- and polydentate ligands and their metal complexes have received less attention,¹⁴ even less for the chelating resins. Recent examples of chelating resins containing sulfur and nitrogen donor atoms are N-(hydroxymethyl) thioamide,¹⁵ thioacetamide,¹⁶ thion-alide,¹⁷ 4-(2-thiazolylazo)-resorcinol,¹⁸ dithizone¹⁹ and so on. 2-Mercaptoethylamine is another popular ligand which coordinates with transition as well as noble metal ions.²⁰ Coates et al. have synthesized several potentially octadentate chelating agents by the reaction of mercaptoethylamine with bisaldehydes.²¹ In this work, we found that the introduction of mercaptoethylamine in the polymeric aldehyde could lead to the production of a novel chelating resin. The aim of the present investigation is to study the complexing behavior of the synthesized resin. The exceptionally high selectivity for noble metal ions in acidic solution suggests that the prepared resin could be an ideal stationary phase of chelation ion chromatography for selective preconcentration and separation of noble metal ions from complex matrix materials, such as various natural water and geological samples.

EXPERIMENTAL

Apparatus

Elemental analyses were carried out with a Perkin Elmer elemental analyzer (model 2400), provided by the Elemental Analyses Service Center of NSC at National Taiwan University. IR spectra of resin or metal-resin complex in KBr pellets were recorded on an infrared spectrophotometer (Perkin Elmer 983). EPR spectra of the complexes in the solid state at room temperature were recorded on a Bruker ESP 300 spectrometer. The electronic spectra were performed with the Hitachi model U-3200 recording spectrophotometer.

Chemical Reagents

Most chemicals were of analytical reagent grade from Merck (Darmstadt, Germany). Purified water (18 M Ω -cm) obtained using a water purification system (Milli-Q Ultrapure Water System, Millipore, USA) was used for all solutions. Most metal salts were purchased from Merck. Chloroauric(III) acid, potassium chloroplatinate(IV) and palladium(II) chloride were obtained from BDH (UK). Stock solutions (ca. 0.1 M) of most metal ions were prepared by dissolving an appropriate amount of the respective metal salt in hydrochloric acid (0.1 M), diluting with pure water to 250 mL, adjusting to pH 1.6 and storing in polyethylene bottles. The concentration of metal ion was verified by EDTA complexometric titration.

XAD-4 (polystyrene-divinylbenzene copolymer) and 2-mercaptoethylamine as the hydrochloride were purchased from Sigma (St. Louis, MO, USA). Hexamethylenetetramine, paraformaldehyde, zinc chloride, sodium iodide, sodium chloride and calcium carbonate were obtained from Merck.

Preparation of Bis(2-aminoethylthio)methylated Resin Chloromethylation of polystyrene-divinylbenzene copolymer

Polystyrene-divinylbenzene copolymer was immersed in an acidic solution (HCl, 6 M) for 1 h. After filtration, the resin was washed with water, methanol and acetone sequentially. The purified material was then ground and sieved to a particle size of 140-230 mesh.

Zinc chloride (10 g) in concentrated hydrochloric acid (37%, 150 mL) was placed in a round-bottom flask. Paraformaldehyde (15 g) and the purified polystyrene-divinylbenzene (15 g) were then added slowly to the reaction flask and heated at 70 °C for 3 days till the resin turned from colorless to pale yellow. The product (P-CH₂Cl) was collected by filtration under suction and washed sequentially with

water and acetone.

Iodomethylation of P-CH₂Cl

Chloromethylated resin, P-CH₂Cl (4 g) obtained by the above procedures was placed in the flask, to which sodium iodide (7.1 g) in acetone (75 mL) was added dropwise. The resultant mixture was reacted under nitrogen at 60 °C for 24 h. The brownish red product (P-CH₂I) was collected by filtration under suction.

Carbonylation of P-CH₂I

P-CH₂I (17 g) was placed in the flask containing hexamethylenetetramine (33.6 g) in ethanol-H₂O (60%; w/v, 130 mL). The resultant mixture was refluxed for 3 days. After cooling, concentrated hydrochloric acid (37%, 50 mL) was added dropwise and the heating was continued for a further 5 h. The product was collected by filtration under suction and washed with water and calcium carbonate aqueous solution (10%; w/v, 100 mL) sequentially. The product is called P-CHO.

Functionalization of P-CHO

2-Mercaptoethylamine-hydrochloride (10.3 g) was dissolved in a mixture of ethanol (95%, 60 mL) and concentrated hydrochloric acid (30 mL). P-CHO (11.3 g) was then added. The resultant mixture was reacted at 50 °C for 3 days till the color of the resin turned from yellow to yellowish-white. After cooling and filtration, the residue was washed with pure water to remove the unreacted 2-mercaptoethylamine. The extent of the washing was verified with the addition of an admixture of sodium azide and iodine, which tests positive for free -SH. In this work, the rate of decolorization was compared with that in a 10⁻⁵ – 10⁻⁶ M solution of 2-mercaptoethylamine.

Preparation of Metal Complexes

Dry resin (ca 300 mg) was added to each polyethylene bottle containing 0.04 M metal ion in pure water with the final volume of 25 mL. The pH of the solution was adjusted to the required value with perchloric acid or sodium hydroxide. The mixture was stirred for 24 h at 25 ± 0.1 °C. After equilibration, the pH value was measured. The solution was then filtered. The metal ion in solution was measured by EDTA titration or spectrophotometry. The wet resin and resin-metal complexes were dried in a vacuum oven and subjected to IR and EPR spectral measurements.

Potentiometric Titrations

Acid dissociation constant

pH-Metric titrations were performed as the procedures in ref. 22 and not as those in the conventional manner. In this investigation, at least 14 samples of the resin (0.2 g) were accurately weighed and placed respectively in each PE

bottle. Aqueous solutions containing various amounts of 0.1 M sodium hydroxide were made to an ionic strength of 0.5 M with potassium chloride and brought to 25 mL total volume. The solutions were added to the PE bottle containing the resin. The mixture was stirred for 4 h at $25 \pm 0.1^\circ\text{C}$. After equilibration, the acidity of the solution was monitored by a Radiometer PHM 61 pH meter with a GK 2401 C combined electrode. pH readings were calibrated before measurements with pH 4.01 and 6.86 standard buffer solutions.

Stability constant

The apparatus and procedures of these experiments were identical to those described in the previous section except that in each case either a 3:1 or 1:1 metal resin-ligand ratio of metal salt was added to the resin solution.

RESULTS AND DISCUSSION

Characterization of the Prepared Resin

The synthetic route for the bis(2-aminoethylthio)methylated resin is shown in Fig. 1. The resin was characterized by elemental analysis, IR spectra, water regain, hydrogen capacity and metal capacity (Table 1). The detailed procedures were carried out according to Reference 23. A relatively more reliable result from nitrogen analysis than that from sulfur analysis was found. Therefore, the functionality of the resin (0.45 mmol g^{-1}) was determined by the results of the former. From the molecular structure, the amount of protonation might be 0.90 mmol g^{-1} . Moreover, the hydrogen capacity of the resin is only 0.68 mmol g^{-1} which is lower than the predicted value. This might be due to partial deprotonation of the functional group under the experimental condition (pH 5-7). The water regain of the resin was determined by centrifugation.²⁴ The water uptake of the resin is a function of pH as shown in Table 1. Since the amino groups of the resin are protonated in the acidic medium and turns to neutral form as the pH increases, the lower the pH of the solution, the easier is the diffusion of the hydrated counter-ion into the resin phase. Hence the water regain is less at higher pH.

The IR spectra of the chloromethylated resin, intermediate and the final product bis(2-aminoethylthio)methylated resin were measured. The most striking spectral evidence for the chloromethylated resin are the aromatic C-H stretching near 3023 cm^{-1} and the aliphatic C-H stretching (2920 cm^{-1}); the aromatic C-C stretching around 1600, 1490, 1450 cm^{-1} and the strong absorption around 900 and 826 cm^{-1} . The aliphatic C-H stretching indicates the presence of substituents in the benzene ring. The C-H out of plane bending

overtone and combination band in the region $2000\text{--}1600 \text{ cm}^{-1}$ are characteristic of different benzene ring substituents. Additionally, a strong band of CH_2 wagging is observed around 1264 cm^{-1} . After carbonylation, a weak intensity at 1264 cm^{-1} was observed. Specific evidence of the aldehyde group was exhibited around 1700 cm^{-1} (C=O) and 2724 cm^{-1} (C-H stretching). Due to overlapping of C-N and C-S with polystyrene around the region of $1450\text{--}1000 \text{ cm}^{-1}$, as well as the fundamental N-H stretching vibrations of NH_2 and NH_3^+ ($3500\text{--}3300 \text{ cm}^{-1}$) with O-H stretching vibration of water in solid state sample ($3600\text{--}3100 \text{ cm}^{-1}$), no significant difference was observed between the carbonylated product and the final product.

Coordination Behavior of the Prepared Resin

The coordination behavior of various transition metal ions with the resin has been investigated with the help of IR, EPR and potentiometry. Compared with the IR spectra of the free resin ligand, a distinct variation in the region $1400\text{--}1200 \text{ cm}^{-1}$ (C-S) and $1200\text{--}1000 \text{ cm}^{-1}$ (C-N) was observed

Fig. 1. The synthesis protocol of the bis(2-aminoethylthio)methylated resin.

Table 1. Physical and Chemical Properties of the Bis(2-aminoethylthio)methylated Resin

Particle size	140-230 mesh
E.A. (%)	C: 84.22; H: 7.59; N: 1.25; S: 1.55
Functionality (mmol g ⁻¹)	0.45
Water regain (g g ⁻¹)	0.21 (pH 2.5); 0.2 (pH 6.6); 0.18 (pH 7.2); 0.17 (pH 8.42); 0.16 (pH 11.0)
Hydrogen capacity (mmol g ⁻¹)	0.68
Copper capacity (mmol g ⁻¹)	0.31 (pH 4.5)
Iron capacity (mmol g ⁻¹)	0.44 (pH 1.8)
Mercury capacity (mmol g ⁻¹)	1.47 (pH 1.5); 1.54 (pH 2.0); 1.71 (pH 2.5)

for all metal complexes. The weaker intensity of metal-resin complexes than the free resin ligand in this region, suggests coordination through the nitrogen and sulfur atoms. The splitting of the C=O band in the Hg-resin complex indicates that the carbonyl is invariably coordinated to mercury(II).

For the determination of metal capacity as a function of pH, a larger excess of metal ion than the resin-ligand is needed. Since noble metal ions are expensive, only metal capacities of other transition metal ions were investigated. The metal ion capacities (mmol g⁻¹) of the resin are Hg(II) 1.81, W(VI) 0.93, Mo(VI) 0.79, Fe(III) 0.44, Cu(II) 0.31, Cd(II) 0.08, Ni(II) 0.06, Zn(II) 0.05, Co(II) 0.04 and La(III) 0.03. Electrorepulsive force between protonated amino group and the metal ion might be the reason for the exceptionally low capacity of the latter group elements. Moreover, metal capacities increase significantly as the pH increases for those higher affinity metal ions, except tungstate and molybdate. The phenomena can be taken into account as a portion of protonated resin-ligand turns to neutral form as the acidity of the medium decreases. A quite large mercury capacity compared to the functionality of the resin was observed (Table 1). The unexpected behavior might be due

to the presence of some metallic state of mercury. Since the reduction potential of mercury is greater than those of iron and copper, the easier reducing phenomenon of mercury(II) by the resin ligand was rational. Meanwhile the iron(III) might be reduced to iron(II) prior to complexation with the resin ligand. In these cases, both copper(II) and iron(II) were found to form a one to one complex with the resin ligand. The assignment was based on the metal capacity and the functionality of the resin.

The sorption property shows that the resin has good selectivity for Ag(I), Au(III), Pd(IV), Pt(IV), Mo(VI), W(VI) and Hg(II). The distribution coefficients of metal ions on the resin at various acidity media are given in Table 2. The resin exhibited distinctly soft properties toward metal ions. As a rule, noble metal ions show a preference for nitrogen and heavy donor atoms (e.g., P, As, S, Se) and relatively small affinity for oxygen donors. The strong binding of the heavy atom donors is due to the formation of metal-ligand π bonds by overlap of filled $d\pi$ orbitals on the metal with empty $d\pi$ orbitals in the valence shell of the heavy atoms. Further it was found that the more acidic the solution, the greater distribution coefficients were demonstrated. Considering the anion exchange property of the resin ligand

Table 2. Distribution Coefficients of Metal Ions on the Bis(2-aminoethylthio)methylated Resin^a

Condition	Distribution coefficient of metal ions (log D)						
	Ag	Au	Cu	Hg	Pd	Pt	Zn
HClO ₄ (6 M)	2.55	3.01	-	2.19	-	3.02	0.01
HClO ₄ (3 M)	2.45	4.68	-	0.61	2.97	3.06	0.52
HClO ₄ (2 M)	2.39	> 5	-	0.13	2.42	3.42	0.49
HClO ₄ (1 M)	2.48	> 5	-	-	1.61	3.90	0.49
pH 2.0	3.35	> 5	-	0.66	0.26	4.32	0.32
pH 3.0	3.19	> 5	0.01	0.90	0.84	4.71	0.29
pH 4.0	-	3.84	0.71	1.26	2.87	2.77	0.33
pH 5.0	-	2.81	-	-	-	-	-
pH 6.0	-	2.19	-	-	-	-	-

^a Amount of resin: 0.3 g; Volume of solution: 25 mL.

($\text{RNH}_3^+\text{Cl}^-$) and the possible anion complex formation of these metal ions at the acidic condition, the results are plausible.

EPR spectroscopy has been widely used in the study of complexes formed between metal ions and various ligands as it offers the potential to define local structure as well as to provide information on the chemical reactions. Spectral studies of copper(II) complexes are of great interest because their states orbitally degenerate in regular geometries and non-degenerate in distorted geometries, since an orbitally degenerate configuration is susceptible to a John-Teller distortion. As a result, EPR studies of copper(II) complexes yield valuable information regarding the nature of bonding between the metal ion and the donor atom. In previous papers,^{22,25} we found that the EPR spectra of copper-hydroxamate resins were dependent on pH and the metal-ligand ratio. In this work, EPR spectra of copper-bis(2-aminoethylthio)methylated resin complexes recorded at room

temperature with various metal-to-ligand ratios were measured (Fig. 2). The parameters are listed in Table 3. The EPR spectra clearly show that $g_{\parallel} > g_{\perp}$, indicating that the unpaired electron of the elongated octahedral or square-planar complex lies in the $d_{x^2-y^2}$ orbitals.²⁶ In the case of 1:1 complex, the copper ion is coordinated through 2N and 2S. Meanwhile, the value of $g_{\parallel}$ less than 2.3 indicates that the metal-ligand bond is covalent in character. If G value > 4.0 , then the local tetragonal axes are aligned parallel or only slightly misaligned; if $G < 4.0$, significant exchange coupling is present and the misalignment is appreciable.²⁶ In the resin phase the EPR spectra of copper ions adsorbed in media of pH greater than 4, provided a distinct different spectra from those in media of pH less than 4. The G value less than 4.0 at a pH value greater than 4 suggests the presence of exchange coupling in these complexes due to misalignment of the coordinate axes of the different copper atoms present in the resin phase. Due to a greater amount of copper being loaded in the resin phase at higher pH media, the phenomena can be explained. Since the EPR parameters correspond to those of the copper(II)-bisthiosemicarbazones²⁷ and copper(II)-thiolato complexes,²⁸ the metal-resin complex might be similar, namely CuN_2S_2 .

Titration curves for the resin ligand and metal-complex formation are provided in Figs. 3A and B. All titration curves of the metal complexes occur at a lower pH than that of resin ligand titration in the absence of metal ion, indicating competition between metal ions and protons to bind with the resin ligand. The acid dissociation constant of the resin and stability constants of the metal-resin complexes were calculated according to a modified Bjerrum's method.²⁹ In this case, only 1:1 metal-resin complex was proposed, owing to the steric hindrance of the polymer matrix. The resin ligand has two protonation constants, and the complexation reactions for these metal ions are described according to the following equilibrium processes and the corresponding equilibrium constants.

Fig. 2. EPR spectra of copper-bis(2-aminoethylthio)-methylated resin complexes. (A) at pH 2.10, Cu(II) loading = 0 mmol g^{-1} ; (B) at pH 2.71, Cu(II) loading = 0.04 mmol g^{-1} ; (C) at pH 3.10, Cu(II) loading = 0.11 mmol g^{-1} ; (D) at pH 3.60, Cu(II) loading = 0.12 mmol g^{-1} ; (E) at pH 3.98, Cu(II) loading = 0.13 mmol g^{-1} ; (F) at pH 4.12, Cu(II) loading = 0.18 mmol g^{-1} ; (G) at pH 4.20, Cu(II) loading = 0.31 mmol g^{-1} .

Table 3. Parameters of EPR Spectra of Copper-resin Complexes as a Function of pH

pH	Capacity ($\mu\text{mol g}^{-1}$)	$g_{\perp}$	$g_{\parallel}$	G^a
2.10	0	2.045		
2.71	40	2.044		
3.10	110	2.043	2.184	4.28
3.60	120	2.049	2.207	4.22
3.98	130	2.051	2.212	4.16
4.12	180	2.068	2.242	3.56
4.20	310	2.076	2.263	3.46
Cu(II)-bisthiosemicarbazone ^b		2.040	2.191	
Cu(II)-N2S2 complex ^c		2.055	2.287	

^a $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$. ^b Ref. 27. ^c Ref. 28.

where $[L]$ is the equilibrium concentration of the resin ligand; $[H_2L^{2+}]$ and $[HL^+]$ are the protonated form of resin ligand; $[X^-]$ is the counter ion of $[H_2L^{2+}]$ and $[HL^+]$; T_L is the total concentration of resin ligand; T_M is the total concentration of metal ion. Bjerrum introduced the concept of the average ligand number to characterize the extent of complex formation, that is the average number of ligands coordinated to one metal ion in a system containing the complex ML . Accordingly, the defining equation is

$$\bar{n} = \frac{T_L - [H_2L^{2+}] - [HL^+] - [L]}{T_M}$$

$$= \frac{2(T_L - [H_2L^{2+}] - [HL^+] - [L])}{[OH^-] + [X^-] - 2[H_2L^{2+}] - [HL^+] - [H^+] - [Na^+]}$$

Substitute $[H_2L^{2+}]$ with $[H^+]^2 [L]/K_1^H K_2^H$ and $[HL^+]$ with $[H^+] [L]/K_1^H$. Following Charberek and Martell's adaption of Bjerrum's method $\bar{n}$, the average number of ligands, bound per mole of metal ion present, was plotted vs. pL , the negative logarithm of resin-ligand concentration calculated from the titration curve. The equilibrium constants determined for the resin ligand (BAETMR) together with those of the correlative monomers,³⁰ ethylenebis(thio-2-ethylamine) (EBTEA), dithiobis(2-ethylamine) (DTBEA), thio-bis(2-ethylamine) (TBEA) and 2-mercaptoethylamine (MEA) are shown in Table 4. Although the repeating unit of the resin ligand is 2-mercaptoethylamine, the geometry of the resin is much more similar to that of EBTEA than the others. Since the polymer matrix is highly rigid, comparison of the stability constants for only one-to-one metal-complex was made. Both dissociation constants and stability constants of the resin ligand are smaller than that of the corresponding monomer. These might be due to steric factors of the polymer matrix, while the selectivity sequence of

the resin coincide somewhat with those of the correlative monomers. The differences in stabilities among these complexes may be attributed to variations in pK_a , ligand flexibility, steric crowding between coordinated ligands and differences in the size of the chelating ring formed. Diphenylthiocarbazone, the reagent being a nitrogen and sulfur donor, is more familiarly known as dithizone. The greater affinity of resin ligand toward mercury(II) could be understandable by comparison with the stability constants of mercury(II)-dithizonate (2×10^{40}), copper-dithizonate (1.5×10^{19}) and zinc(II)-dithizonate (9×10^{13}).³¹

Fig. 3. Titration curves for bis(2-aminoethylthio)methylated resin alone and in the presence of metal ions at $25 \pm 0.1^\circ \text{C}$ and ionic strength of 0.5 M KCl. $[HCl] = 0.1000 \text{ M}$, $[NaOH] = 0.0799 \text{ M}$. (A) $C_L/C_M = 3:1$; (B) $C_L/C_M = 1:1$.

Table 4. Equilibrium Constants of Resin Ligand, Correlative Monomers and Their Metal Complexes

Metal ion	Equilibrium	log K				
		BAETMR ^a	EBTEA ^b	DTBEA ^d	TBEA ^c	MEA ^f
H ⁺	HL/H-L	8.53	9.53	9.04	9.50	10.69
	H ₂ L/HL-H	6.87	8.70	8.70	8.70	8.28
Fe(III)	ML/M-L	12.0				
Co(II)	ML/M-L	3.76	4.50		5.09	7.68
	ML ₂ /M-L ²		7.61		9.01	14.71
Ni(II)	ML/M-L	3.78	7.41		7.27	10.05
	ML ₂ /M-L ²		7.69 ^c		13.37	19.81
Cu(II)	ML/M-L	7.75	10.70	6.70	9.07	
	ML ₂ /M-L ²		10.91 ^c		14.15	
Zn(II)	ML/M-L	5.07	4.96		5.31	10.22
	ML ₂ /M-L ²		9.06		8.88	18.90
Cd(II)	ML/M-L	4.17	5.31		5.47	10.97 ^g
	ML ₂ /M-L ²				8.99	19.75 ^g
Ag(I)	ML/M-L		8.34			
Hg(II)	ML/M-L	13.05				

^a Bis(2-aminoethylthio)methylated resin (BAETMR) measured at 25 °C, $\mu = 0.5$ M KCl.^b Ethylenebis(thio-2-ethylamine)(H₂NCH₂CH₂SSCH₂CH₂SSCH₂CH₂NH₂)(EBTEA) measured at 25 °C, $\mu = 0.1$ M.^c At 25 °C, $\mu = 0.5$ M.^d Dithiobis(2-ethylamine)(H₂NCH₂CH₂SSCH₂CH₂NH₂)(DTBEA) measured at 20 °C, $\mu = 0.15$ M.^e Thiobis(2-ethylamine)(H₂NCH₂CH₂SSCH₂CH₂NH₂)(TBEA) measured at 30 °C, $\mu = 1.0$ M.^f 2-Mercaptoethylamine (HSCH₂CH₂NH₂)(MEA) measured at 30 °C, $\mu = 1.0$ M.^g At 25 °C, $\mu = 0.1$ M; ^a This work; ^{b-g} Ref. 30.

CONCLUSIONS

A novel chelating resin containing sulfur and nitrogen donor atoms was prepared and characterized. Some coordination behavior, such as metal ion capacities, distribution coefficients and stability constants determined are highly useful to estimate their selectivity and analytical potentialities. For the greater reduction potential of soft metal ions than other transition metal ions, an easier reducing phenomenon by the resin ligand was found. This yields an unexpected large metal capacity compared to the functionality of the prepared resin. Alkali and alkaline earth metals are not retained on the resin over a wide acidity range, which is of advantage from the viewpoint of possible applications of the resin to the analysis of trace metal ions in natural water and biological materials. With this highly selective resin as stationary phase of chelation ion chromatography, the concentration and separation of noble metal ions from other transition metal ions are ideally suited. Analytical application of this resin is now in progress.

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Key Words

Chelating resin; 2-Mercaptoethylamine; Coordination behavior.

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