Journal of the Chinese Chemical Society, **1996**, *43*, 473-478

Chelating Properties of γ-Aminobutyrohydroxamate Resin toward Lanthanides

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γ-Aminobutyrohydroxamate resin that simulate siderophore analogues was prepared. The structure and conversion of functional groups of the resin were confirmed with IR spectra and elemental analysis. The influence of pH on adsorption of metal ions to the resin was examined. Uptake of metal ions increased with pH and was quantitative in the pH range of 4 to 6 for most of the lanthanides. These metal ions showed high exchange rates towards the resin. The complexation behavior of the resin was also investigated by means of IR and potentiometry. The dissociation constant, pK_a of the hydroxamic hydroxyl group is 9.36. Stability constants of the insoluble lanthanide complexes on the resins were measured potentiometrically at 25 ± 0.1 °C and ionic strength of 0.1 M KCl. The results were compared with those of the corresponding soluble lanthanide complexes. It was found that a higher stability of the resin resulted in an increase of the stability constants. The phenomena might be due to the length of the spacer in providing the proper geometry of the resin ligand for intramolecular metal complexation.

INTRODUCTION

Rare earths are important elements not only in industrial applications but also concerning energy and environmental problems.[1] Currently several methods of analysis have been used for the determination of rare earth elements in geological materials or biological samples. Among them neutron activation analysis (NAA), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) have been most widely used. However, environmental and geological materials represent exceptionally complex matrices, giving rise to interelement effects or mutual spectral interferences, that can cause errors in the determination. ICP-MS is a relatively sensitive technique, that allows the direct analysis of samples without the need for separation or preconcentration,[2,3] but it is expensive and much more fundamental research is needed to improve its performance, reliability and accuracy.[4]

Nowadays, ion chromatography is routinely employed in the determination of the great variety of organic and inorganic ionic species, although initially it was targeted for inorganic analysis. As trace metal analysis using conventional ion chromatography becomes very difficult with samples of high ionic strength such as concentrated brines and sea-waters, it requires special methods such as using chelating substances.[5-9] Chelation ion chromatography (CIC) first reported by Kingston et al.,[5] has become a very powerful technique for trace and ultra trace ion analysis in complex matrices.

Hydroxamic acids are one kind of chelating molecules which are being used extensively in analytical chemistry. We recently prepared several new chelating resins analogous to siderophores.[10-12] Some of these have found use as the stationary phase of chelation ion chromatography for the determination of metal ions in the complex matrix samples.[13,14] In continuous of our current studies in this area with chelating resins exhibiting highly selective properties, we have investigated the chelating properties of γ-aminobutyrohydroxamate resin toward lanthanides and their potential for the determination of lanthanides in complex matrix samples.

EXPERIMENTAL SECTION

Apparatus

Infrared spectra of a resin or a metal-resin complex in KBr pellets were recorded on a Perkin-Elmer 983 infrared spectrophotometer. UV-vis spectra were measured on a Hitachi model U-3200 recording spectrophotometer. A Radiometer pH meter (Copenhagen, Denmark, PHM 61) was used to measure pH values. The electrode was checked against Merck Buffer-Titrisol (pH 4.00 and 7.00).

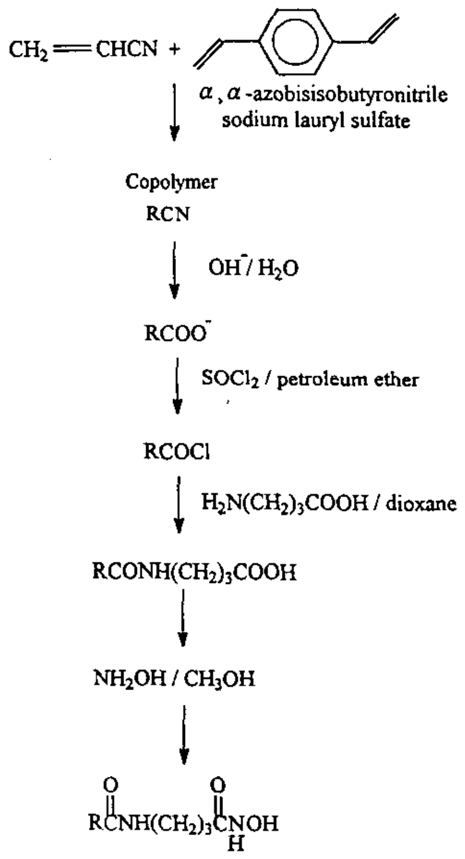
Chemicals

Most chemicals were of analytical reagent grade (E. Merck, Darmstadt, Germany). Purified water (18 MΩ-cm) using a water purification system (Milli-Q Ultrapure Water System, Millipore, USA) was used for all solutions. Stock solutions of lanthanide chlorides were prepared by dissolution of 99.99% pure samples of the respective oxides (Ln_2O_3) (Merck, Darmstadt, Germany) in hydrochloric acid. The excess hydrochloric acid was evaporated to near dryness. Then a known amount of hydrochloric acid was added to the residue and diluted to a definite volume in a volumetric flask to bring the final pH into the 2-3 range. The concentration of metal ion was verified by EDTA complexometric titration.

Preparation of Chelating Resins

The γ-aminobutyrohydroxamate resin was prepared by a method (Scheme I) as previously described.[5]

Scheme I Preparation of the γ-aminobutyrohydroxamate resin



Determination of the Adsorption Capacity

A batchwise technique was employed to determine the equilibrium adsorption capacity with the metal ion being in excess over the ligand content. Typically, 0.3 g of the dry resin was added to 25 mL of metal ion solution (0.04 M) of various pH values. After shaking for two days at 25 °C the pH at equilibrium and the amount of metal ion remaining in the solution were determined. The wet resin phase was dried in a vacuum oven and IR spectral measurements were made.

Distribution Coefficients

The equilibrium distribution coefficient of the metal ion was also determined with a batchwise procedure. 0.3 g of dry resin was immersed in 25 mL of metal ion solution (0.0004 M). The equilibrium pH and the amount of metal ion in solution were determined.

Potentiometric Titrations

Acid dissociation constant

Dissociation constants for the resin ligand were known from previous work.[5] The titrations were run at 0.1 M KCl and 25 ± 0.1 °C. After equilibration, the pH was measured.

Stability constant

At least 14 samples (0.2 g) of the resin were weighed accurately and each placed into a PE bottle (100 mL). Aqueous solutions containing various amounts of NaOH (0.1 M) and metal ion at a 1:1 or 1:3 metal to resin ligand ratio were made up to ionic strength of 0.1 M with KCl and then brought to 25 mL total volume. The solutions were then added to the resin. The mixture was stirred for 4 h at 25 ± 0.1 °C. Experimental procedures for the titrations were as in the titrations of the free resin ligand, which were carried out in batch system and each sample were run in duplicate. To avoid precipitation in higher pH ranges, experiments were carried out below pH 7.

RESULTS AND DISCUSSION

Chelating behavior of resin toward lanthanides

The γ-aminobutyrohydroxamate resin was prepared (Scheme I), and characterized by elemental analysis, IR spectra, water regain (1.97 g per gram resin), hydrogen capacity (2.21 mmol per gram resin for the hydroxamate group and 3.82 mmol per gram resin for the unreacted carboxylate group) and metal capacity (1.50 mmol per gram resin for copper at pH 4.0) in accordance with our previous work.[10,12,15] The chelation property toward first series transition metal ions has been reported.[12] Since the prepared resin with 8% cross linking is insoluble in common solvents, no information of the molecular weight was obtained. So the results of the elemental analysis for carbon, 45.85%; hydrogen, 6.86%; and nitrogen, 6.83% were used only to confirm the conversion of the carboxylate resin to the hydroxamate resin.

The capacity-pH profiles for lanthanides are given in Fig. 1. Here a large excess of metal ion relative to the amount of resin was used to observe maxima in the metal uptake as a function of pH. The adsorption capacity apparently depends on the pH of the solution, due to the competing protonation and complexation reactions of the functional group. The maximum capacity is approximately 1.7 mmol g^{-1} at pH greater than 5.0 irrespective of the metal ions examined. This value is close to the estimated ligand content (2.21 mmol g^{-1}). Hence the functional group in the resin appears to form a one to one complex with these metal ions.

The uptake of metal ions with resin ligand in large excess as a function of pH was also studied. The results could offer us useful information necessary for quantitative removal of metal ions from solution with either batch or column methods. Distribution coefficients between the aqueous phase and resin phase indicate that all extraction of lanthanides attained nearly 100% at pH greater than 4. However, the formation of soluble hydroxo metal chelates were found at pH greater than 6. Hence the capacity decreased significantly. The phenomena were most distinct in the case of Eu, Dy, Ho and Er among the lanthanides tested. Only 40-50% sorption was found for these metal ions and 80% for La and Tb at pH 9. There was no apparent change in the sorption for Ce, Pr, Nd, Sm and Gd at the medium of greater pH value. The results might be normal, since the formation constants between OH^- and lanthanide increase with the increasing of atomic number.[16] The compromise condition for preconcentration trace amount of lanthanides is in the pH range of 3-7.

IR spectra of the γ-aminobutyrohydroxamate resin and its lanthanide complexes were measured. The absorption band near 3300 cm^{-1} is assigned to the N-H and O-H stretching mode, whereas those in the region 3080-3060 cm^{-1} are attributed to the overtone of amide II band. Specific evidence of covalently bound hydroxamate is provided by infrared absorption of the ketonic carbonyl and intramolecular hydrogen bonding of hydroxamate groups about 1700-1650 cm^{-1}. Coordination of hydroxamate caused the absorption to shift towards smaller wavenumbers and the peak intensity decreased. Lines in the region near 1445 cm^{-1} are assigned qualitatively to the N-C stretching vibration with contributions from C-O and C-R modes, those about 1300 cm^{-1} to C-R stretches, and those about 1100 cm^{-1} to a practically pure

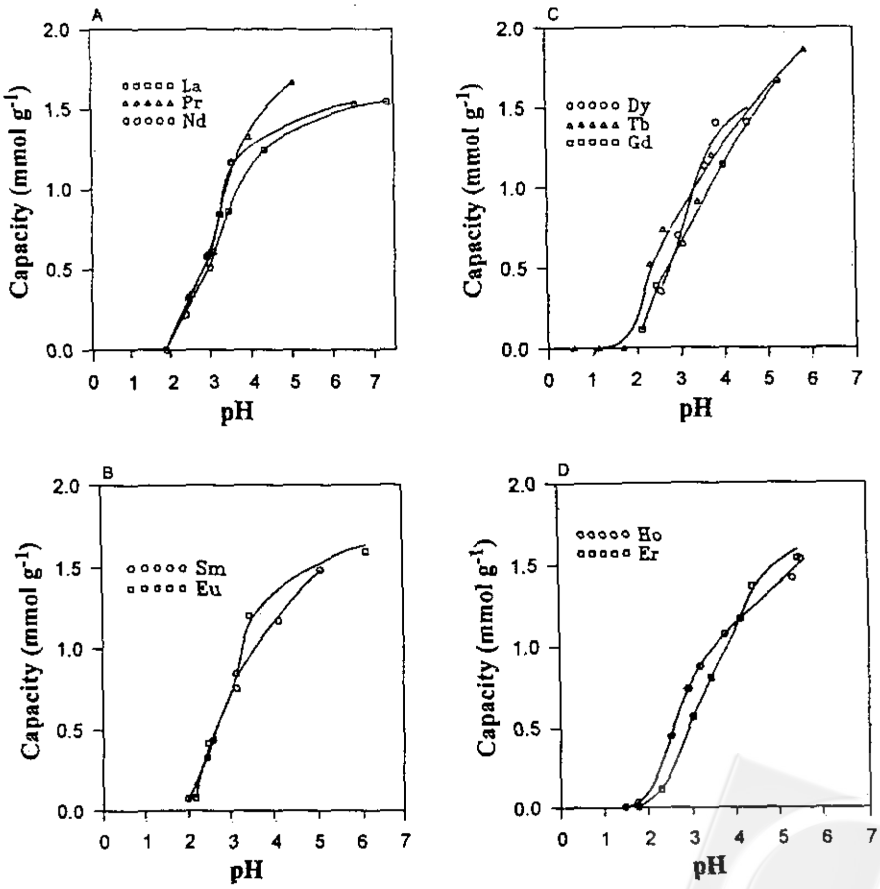


Fig. 1. Metal capacity as a function of pH. Amount of metal ion: 10 mmol; Amount of resin: 0.3 g; Volume of solution: 25 mL. A. La (□), Pr (Δ), Nd (o); B. Sm (o), Eu (□); C. Dy (o), Tb (Δ), Gd (□); D. Ho (o), Er (□).

N-O stretching mode. As the metal capacity increased, two new peaks near 1590 and 1520 cm^{-1} appeared and the peak intensity in the region around 1410, 1450 and 1100 cm^{-1} is more pronounced. The peak intensity of lines in the region near 1230 and 900 cm^{-1} decreased and shifted towards larger wavenumbers for the metal complexes. Some possible M-O stretches are observed in the region < 600 cm^{-1}, but assignment is difficult.

For analytical applications, chelating resins mainly suffer from two short comings, slow uptake of metal ions due to steric hindrance of the dense polymeric matrix and lower activity of the ligands situated at the inside of resins.[17] Chelating resins as a rule tend to be kinetically inferior to conventional resins due to the mechanism of both chemical reaction and ion exchange. The rates of metal ion uptake were measured with the resin in a batch process. Results from experiments with La(III) and Ce(III) are shown in Fig. 2. The half-extraction times for these metal ions on the resin were less than one minute. Contrary to other sorbents with similar groups, the prepared sorbent possesses proper kinetic properties, which is a promising property for chromatographic usage. The possibility of desorbing metals was also studied; solutions of HCl and HNO_3 were used for this purpose. It was found that the metal ions were completely desorbed with 3 M HCl.

Proton-resin equilibria

Acidic and basic properties of chelating resins are generally characterized by determining the content of chelating groups and the dissociation constants. The dissociation constants of the γ-aminobutyrohydroxamate resin determined by potentiometry has been reported.[10] As shown in Fig. 3, the potentiometric titration curve shows two buffer regions. The first one is the neutralization point of the unreacted carboxylic acid, whereas the second region is most likely associated with the neutralization of the hydroxamate group of the resin. The stepwise dissociation constants amount to $pK_a = 4.75$ for the carboxylic acid group and $pK_a = 9.36$ for the hydroxamic hydroxyl group. In comparison the dissociation constants of the desferrioxamin B analogue are $pK_{a1} = 8.39$, $pK_{a2} = 9.03$, and $pK_{a3} = 9.70$.[18] Desferrioxamin B is a siderophore which contains three hydroxamate groups covalently linked to a linear framework. The important feature of the siderophore is that the three hydroxamate groups can bind to a single Fe(III) ion to give a neutral, water soluble, six oxygen-donor octahedral complex of high spin configuration which is kinetically labile.[19] Differences between the dissociation constant of the resin and the model compound is apparently due to different structural parameters.

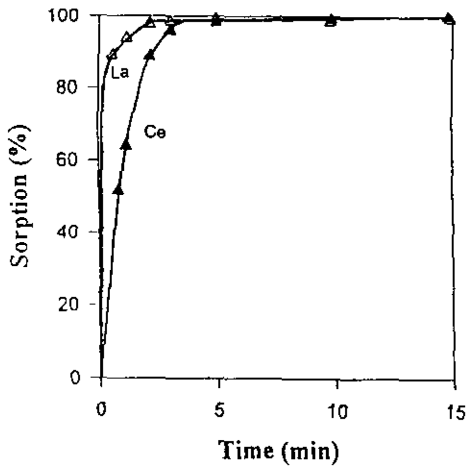


Fig. 2. Sorption rate of metal ion on γ-aminobutyrohydroxamate resin. Amount of metal ion: 0.1 mmol; Amount of resin: 0.3 g; Volume of solution: 25 mL at acetate buffer (0.1 M, pH 5.0); Temp: 25 ± 0.1 °C.

Lanthanide-resin complexes

The stability of complexes formed in the phase of chelating resins is characterized by means of calculated stability constants. Generally, stability constants of insoluble complexes are studied by the ligand competition method, the metal competition method, the proton competition method and the pH of the decomplexation method.[15] The values of stability constants are approximate, but they are extremely useful for estimation of the selectivity of chelating resins and their analytical potentialities. Titration curves for the metal-resin complex appear in Fig. 3. All titration curves of the metal complexes occur at a lower pH than that of ligand titration in the absence of metal ion, indicating competition between metal ions and protons to bind with the resin ligand. The complexation reactions for these metal ions can be described according to the following equilibrium processes and the corresponding equilibrium constants.

$$M^{n+} + HL \overset{K_{f1}}{\rightleftharpoons} ML^{(n-1)+} + H^+$$

$$ML^{(n-1)+} + HL \overset{K_{f2}}{\rightleftharpoons} ML_2^{(n-2)+} + H^+$$

$$ML_2^{(n-2)+} + HL \overset{K_{f3}}{\rightleftharpoons} ML_3^{(n-3)+} + H^+$$

Bjerrum[20] introduced the concept of the average ligand number, $\bar{n}$, to characterize the extent of complex formation. The average number of ligands coordinated to one metal ion in a system containing the series of complexes ML, ML_2 and ML_3, accordingly, the defining equation is

Table 1. Equilibrium Constants for Lanthanide - γ-Aminobutyrohydroxamate Resin Complexes

Metal ion	$\log K_{f1}$	$\log K_{f2}$	$\log K_{f3}$	$\log \beta$
La(III)	9.39 (5.16)[a](10.89)[b]	9.38 (4.17)[a](6.42)[b]	9.20 (2.55)[a](6.02)[b]	27.97 (11.88)[a](23.33)[b]
Ce(III)	9.75 (5.45)[a]	9.53 (4.34)[a]	9.40 (3.01)[a]	28.68 (12.80)[a]
Pr(III)	9.51	9.50	9.24	28.25
Nd(III)	9.72	9.65	9.38	28.75
Sm(III)	9.65 (5.96)[a]	9.65 (4.77)[a]	9.45 (3.68)[a]	28.75 (14.41)[a]
Eu(III)	9.62	9.58	9.34	28.54
Gd(III)	9.70 (6.10)[a]	9.57 (4.76)[a]	9.26 (3.07)[a]	28.53 (13.93)[a]
Tb(III)	9.71	9.49	9.10	28.30
Dy(III)	9.71 (6.52)[a]	9.48 (5.39)[a]	9.06 (4.04)[a]	28.25 (15.95)[a]
Ho(III)	9.69	9.49	9.24	28.42
Er(III)	9.69	9.46	9.22	28.37

[a] The stability constants of lanthanide-acetohydroxamate complexes at 20 °C and ionic strength of 0.1 M.[18]

[b] The stability constants of lanthanide-desferrioxamin B complexes at 20 °C and ionic strength of 0.1 M.[18]

$$\bar{n} = \frac{T_L - [L]}{T_M} = \frac{[ML^{(n-1)+}] + 2\,[ML_2^{(n-2)+}] + 3\,[ML_3^{(n-3)+}]}{[M] + [ML^{(n-1)+}] + [ML_2^{(n-2)+}] + [ML_3^{(n-3)+}]}$$

in which T_L and T_M are the total concentrations of ligand and metal ion, respectively, and [L] is the equilibrium concentration of the ligand. The difference between T_L and [L] is therefore the concentration of the bound ligand.

By ploting $\bar{n}$ against pL, we can read approximate values of $\log K_{f1}$, $\log K_{f2}$ and $\log K_{f3}$ directly from the graph. All lanthanides form strong complexes with the resin (Table 1). The results show that the stability constants vary little among the metal ions tested. The metal-ligand interaction does not increase significantly with decreasing lanthanide radius. In general, stability constants of chelating resins are smaller than those of monomeric ligand because of steric limitations imposed by the polymeric structure of the resin or large energy expenditures needed to complex chelating resins. However, the stability constants obtained for the insoluble resin complexes shows that they are rather stable, probably because of the appropriate chain length of the

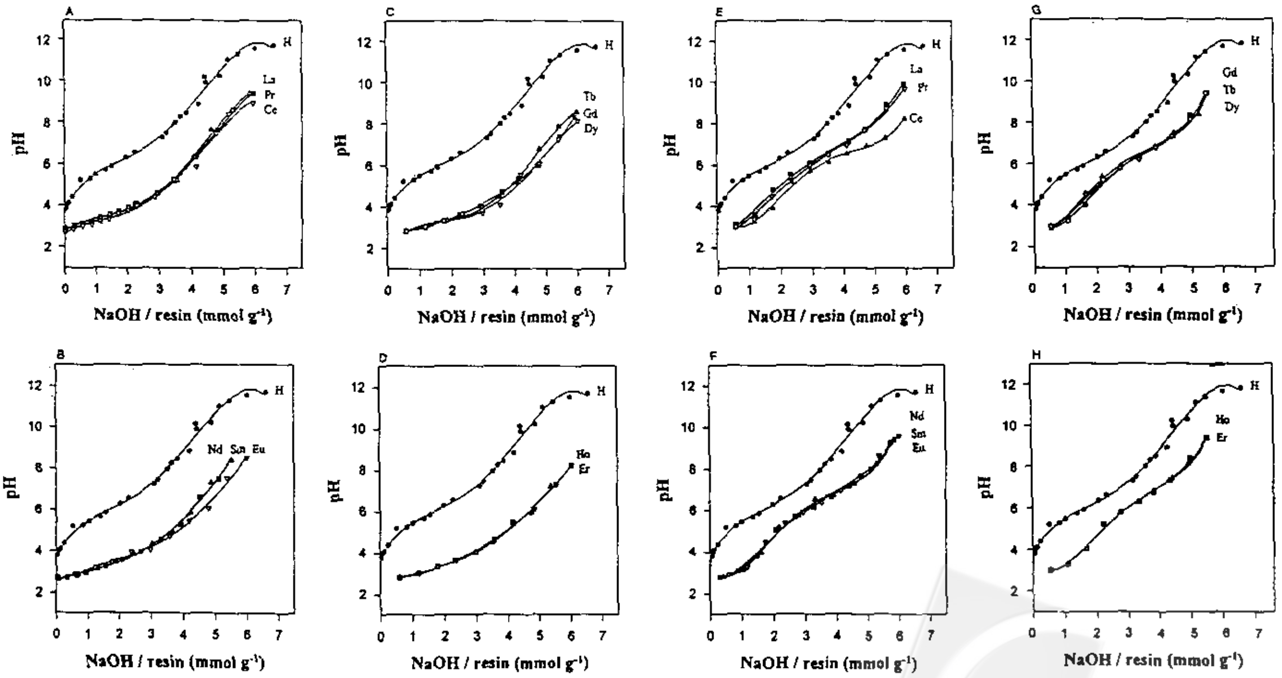


Fig. 3. Titration curves of γ-aminobutyrohydroxamate resin. Amount of resin: 0.2 g; Volume of solution: 25 mL; Ionic strength: 0.1 M KCl; Temp.: 25 ± 0.1 °C. A, B, C, and D: $C_L/C_M = 1$; E, F, G, and H: $C_L/C_M = 3$.

spacer, thus leaving an available environmental condition for the intramolecular metal complexation.[10]

CONCLUSION

The varied stability of complexes formed in the resin phase during sorption at different pH medium is reflected in their selectivity for individual elements. This feature serves as the basis for selective concentration and separation of elements. The selectivity series is the same as that from sorption and metal capacity. In this investigation, the dissociation constants of the resin and the stability constants of metal-resin complexes were determined under conditions different from those in homogeneous solution.[10] The synthesized resins have been shown to be useful in the recovery of lanthanides because of their high adsorption capacity and rapid adsorption rate, although the differences of the stability constants among the lanthanides are not sufficiently large for chromatographic separation. We intend to conduct combination methods on the separation of lanthanides using this chelating resin.

ACKNOWLEDGMENT

We thank the National Science Council of the Republic of China for financial support.

Received October 30, 1996.

Key Words

Chelating properties; γ-Aminobutyrohydroxamate resin; Lanthanides.

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