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Separation of Ions on Columns of Cerium(IV) Silicate, A New Ion Exchanger

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ABSTRACT

Six different samples of a new inorganic ion exchanger, cerium(IV) silicate, have been prepared under varying conditions. Ion-exchange capacity, IR, X-ray, thermogravimetry, composition, and distribution coefficients of many metal ions have been studied and discussed. Separations of Cr^{III}–V^{V}, Cu^{II}–Bi^{III}, Ti^{IV}–Cr^{VI}, and Cr^{III}–Cr^{VI} have been developed on columns of this ion exchanger.

INTRODUCTION

Synthetic inorganic ion exchangers have found wide use in separation science due to their selectivity toward certain elements (1). They are also stable both chemically and thermally. Silicates form one of the most important classes of these ion-exchange materials with applications in nuclear and enviromental areas (2–8). In continuation of our work on the synthesis of some new inorganic ion exchangers (4, 5, 9, 10), we found cerium(IV) silicate to have useful ion-exchange properties. The present paper describes the synthesis, ion-exchange properties, and analytical applications of cerium(IV) silicate.

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EXPERIMENTAL

Reagents

All the chemicals used were from E. Merck (Analytical Grade).

Apparatus

pH measurements were made with a Schott CG841 pH-meter (Germany). A Perkin-Elmer IR-843 Spectrometer was used for IR studies. X-ray studies were made with a Jeol Model GDX-8030 (Japan). Thermogravimetric analysis was performed on a Dupont Model 951. Quantitative determinations of inorganic ions were carried out using an atomic absorption spectrometer (AAS, Model 20 Varian) and an inductively coupled plasma spectrometer (ICP, Model 5500 Perkin-Elmer).

Preparation of Cerium(IV) Silicate

Six samples of cerium(IV) silicate were prepared by gradually adding sodium silicate solution to cerium(IV) sulfate solution under the various conditions given in Table 1. While the reaction mixture was thoroughly stirred with a magnetic stirrer, the pH of the system was increased slowly by adding NaOH or NH_4OH to the desired final pH for completion of gel formation. The gel formed was allowed to settle overnight. It was then filtered off and washed five times with demineralized water and dried in an oven at 50°C. The samples were finally converted into the H^+ form using 1 M HNO_3.

TABLE 1
Synthesis and Properties of Cerium(IV) Silicate

		Analytical data				Cation-exchange capacity (meq/g)		
Sample	Sample code	Concentration of reagents (M)	Mixing volume ratio, Ce : Si (v/v)	Gel,[a] final pH	Composition, Ce/SiO_3	pH 3	pH 9	pH 11
1	CS-1	0.05	1 : 2	7.9	0.91	0.6	1.0	1.6
2	RCS-1[b]	0.05	1 : 2	12.1	0.96	0.1	0.9	1.6
3	CS-2	0.05	1 : 2	5.1	1.27	0.5	1.0	1.8
4	CS-3	0.1	1 : 1	8.4	2.20	0.3	0.9	1.9
5	CS-4	0.1	1 : 3	9.0	0.60	0.6	1.2	2.2
6	CS-6[c]	0.05	1 : 3	9.2	0.92	0.4	1.1	1.9

[a] The pH was adjusted by adding NaOH or NH_4OH solutions for completion of gel formation.
[b] Refluxed in mother liquor for 24 hours.
[c] Refluxed in mother liquor for 2 hours.

Ion-Exchange Capacity

The cation-exchange capacity of each sample was determined using $NaNO_3$ solution at different pH values according to the reported methods (11, 12).

Composition

250 mg portions of the ion-exchanger samples were decomposed in 10 mL hot 4 M NaOH and then digested in dilute HNO_3 (1 : 1). Cerium and silicon were determined volumetrically (13) and by atomic absorption methods (14), respectively.

Distribution Coefficients

The distribution coefficients (K_d) of metal ions in aqueous media were determined by batch operation (15). 200 mg of an ion exchanger (CS-1, RCS-1, CS-2, CS-3, CS-4, CS-6) was equilibrated at 25 ± 0.1°C in 20 mL of 1.25×10^{-4} M metal ion solution. The metal ions were determined with AAS or ICP (16) methods.

RESULTS

X-Ray Analysis

X-ray diffraction patterns show that all the samples are noncrystalline except sample RCS-1 which is weakly crystalline in nature.

Infrared Absorption Spectra

IR spectra of samples were measured by the standard KBr disc technique. The IR spectrum of Sample CS-4 is recorded in Fig. 1.

pH Titration

The pH titration of the ion exchanger was performed by the method of Topp and Pepper (17). The pH-titration curve of Sample CS-4 is given in Fig. 2.

Thermogravimetric Studies

Thermogravimetric analysis of various samples was carried out with a heating rate of 10 K/min. The thermogram for Sample CS-4 in H^+ form is recorded in Fig. 3.

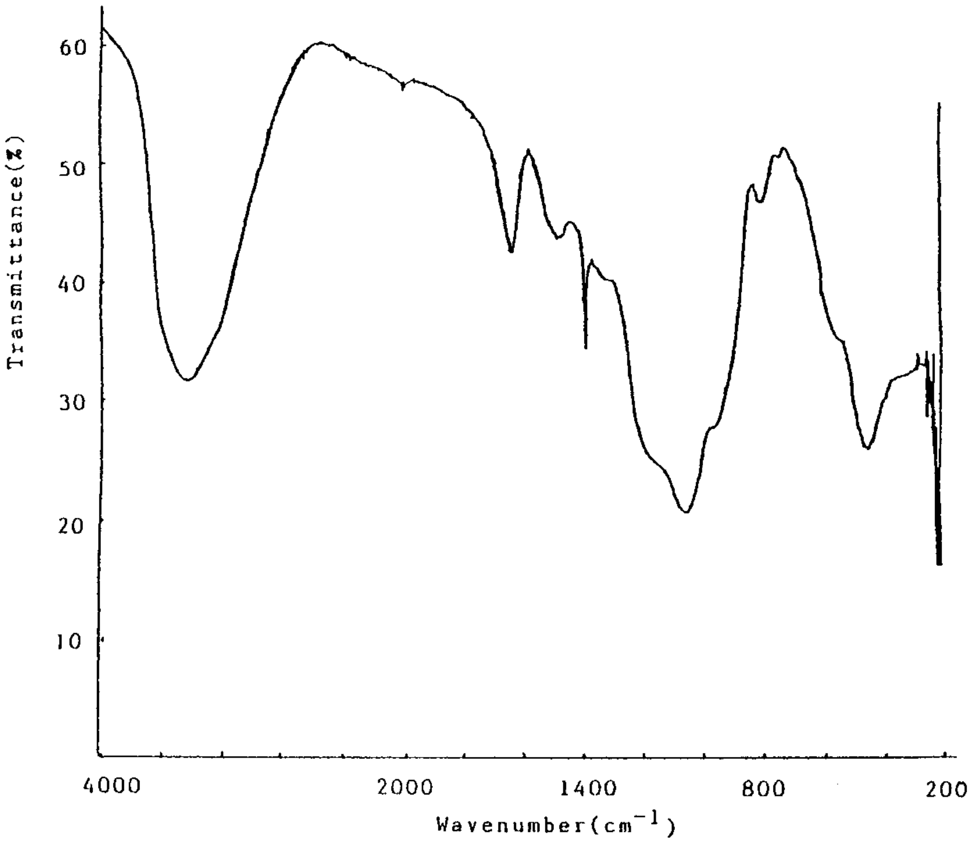

FIG. 1 Infrared spectrum of cerium(IV) silicate (CS-4).

Chemical Stability

All six samples are stable in water, dilute mineral acids, ethanol, methanol, acetone, and ether. However, when heated in concentrated HCl and 4 M HNO_3 or 4 M NaOH, they gradually decompose.

DISCUSSION

The properties of inorganic ion exchangers vary widely by changing the conditions of their preparation (9, 10, 18). The mode of preparation has a significant effect on the size and shape of the cavities inside the exchanger and its chemical stability. Six different samples of cerium(IV) silicate were prepared under various conditions.

The infrared spectrum of cerium(IV) silicate recorded in Fig. 1 can be explained on the basis of IR data for silicates (4, 6, 15). The first band with

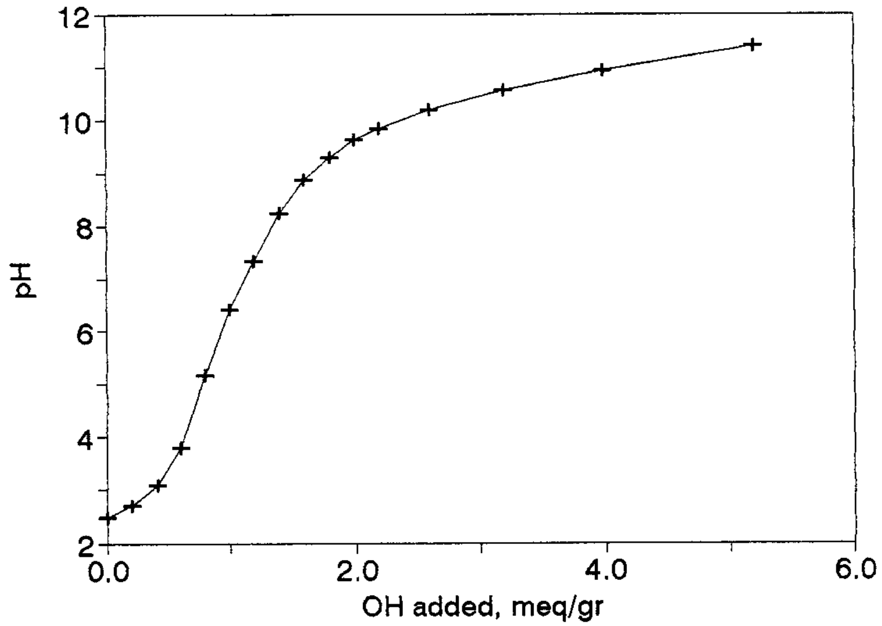

FIG. 2 pH–titration curve for cerium(IV) silicate (CS-4) ion exchanger.

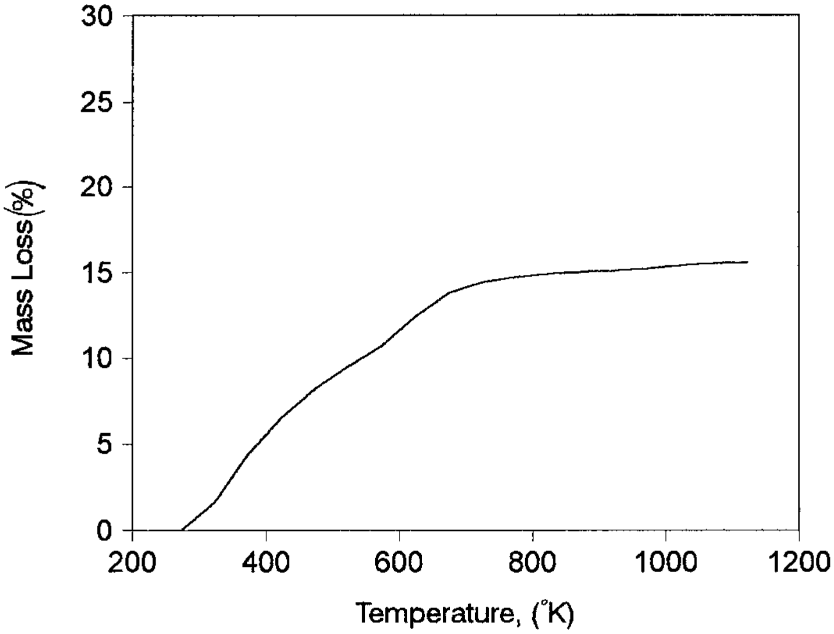

FIG. 3 Thermogram of cerium(IV) silicate (CS-4).

a maximum at 3440 cm^{-1} is due to interstitial water and hydroxyl groups. The sharp peak at 1610 cm^{-1} is due to the deformation vibration of the free water molecules. The very sharp peak at 1400 cm^{-1} is due to the presence of nitrate ion (19), which supports the amphoteric behavior (20), here shown by cerium(IV) silicate ion exchanger. The band at 1020 cm^{-1} and a peak at 800 cm^{-1} are characteristic of silicates. The peak at 440 cm^{-1} is associated with the metal—oxygen bond.

The pH-titration curve of the ion exchanger recorded in Fig. 2 shows one inflection point, indicating that the ion exchanger behaves as a monobasic acid. It is inferred from the curve that the ion exchanger is not appreciably hydrolyzed in acid media. There is a corresponding increase in the pH of the solution with a slow increase in the OH^- concentration.

The thermogram for Sample CS-4 in H^+ form is recorded in Fig. 3 and can be explained as follows; Up to 383 K the mass loss is due to removal of free external water molecules. Condensation of exchangeable hydroxyl groups takes place from 383 to 673 K which is the usual behavior of synthetic inorganic ion exchangers (6). Above 673 K the gradual loss in mass is probably due to the formation of oxides of cerium (9). The curve pattern shows that it is a stable ion exchanger up to 900 K.

X-ray studies of all samples at 298 K give XRD patterns which show that they are noncrystalline, except for Sample RCS-1 which is weakly crystalline in nature. However, after calcination, the x-ray diffraction patterns of the samples show that their crystallinity is slightly improved between 773 and 1073 K, while Sample RCS-1 shows an improved semicrystalline pattern. (Powder x-ray diffractograms are not included to save space.)

The distribution coefficients of inorganic ions on this ion exchanger (Table 2) show good selectivity of this material for a number of ions in water. On the basis of the results recorded in Table 2 it may be inferred that cerium(IV) silicate behaves as a good anion exchanger in the low pH range, showing a high affinity for anionic species and also a weak uptake of cationic species, resulting in low K_d values for a number of elements. This is supported by an increase of the cation-exchange capacity of cerium(IV) silicate ion exchanger at high pH values (Table 1). Amphoteric ion exchangers act as anion exchangers at low pH values and act as cation exchangers in the high pH range (20). The utility of this ion exchanger has been demonstrated by achieving separations of great analytical significance. For example, Cr^{VI} was separated from Cr^{III} and Ti^{IV} (Figs. 4 and 5). The presence of Cr^{VI} and its separation from Cr^{III} in water is of prime environmental importance (21). Here Cr^{VI} is highly adsorbed on the column at acidic pH (Table 2) as an anionic species, while Cr^{III} and Ti^{IV} are passed through the column as cations due to their low K_d values. Later, by using an ammonia solution, Cr^{VI} is eluted from

TABLE 2

Distribution Coefficients of Elements on Cerium(IV) Silicate: K_d Values (mL/g) for Different Samples[a]

Metal ion	CS-1	pH[b]	RCS-1	pH[b]	CS-2	pH[b]	CS-3	pH[b]	CS-4	pH[b]	CS-6	pH[b]
Be^{II}	2.7	2.35	4.6	2.32	4.5	2.80	4.6	2.64	4.7	2.37	10.3	2.63
Ti^{IV}	9.2	1.59	3.9	1.59	16.8	1.61	8.8	1.64	10.4	1.60	35.7	1.61
V^{V}	103	2.34	71	2.26	460	2.72	274	2.63	320	2.30	>5000	2.56
Cr^{III}	14	2.32	13	2.26	18.4	2.69	16.7	2.58	15.1	2.31	5.1	2.53
Cr^{VI}	2830	2.43	483	2.37	80	3.12	70	2.99	4570	2.41	>5000	2.76
Co^{II}	N.A.	2.32	N.A.	2.25	N.A.	2.68	N.A.	2.64	N.A.	2.30	0.2	2.54
Ni^{II}	1.7	2.36	2.35	2.30	3.2	2.81	3.3	2.67	1.5	2.34	2.5	2.63
Cu^{II}	N.A.	2.35	N.A.	2.34	N.A.	2.79	N.A.	2.68	N.A.	2.35	2.1	2.62
As^{III}	220	2.42	65	2.34	83	3.01	56	2.80	260	2.38	2173	2.73
Se^{IV}	2800	2.42	1524	2.35	2380	3.01	3765	2.85	3770	2.41	4820	2.79
Zr^{IV}	16	2.31	21.0	2.23	101	2.60	25.5	2.58	18.5	2.28	39.3	2.54
Ag^{I}	59	2.32	42	2.24	42	2.64	37.9	2.54	76	2.30	1597	—
Cd^{II}	N.A.	2.32	1.5	2.24	4.6	2.63	4.0	2.58	2.7	2.30	6.0	2.54
Sb^{V}	148	1.67	120	1.64	304	1.69	106	1.70	211	1.67	>5000	1.68
Te^{IV}	704	2.44	312	2.38	3500	3.15	1687	2.84	440	2.46	>5000	2.85
W^{VI}	870	2.43	587	2.34	752	3.02	380	2.82	2900	2.38	>5000	2.82
Hg^{II}	3.6	2.28	N.A.	2.21	27	2.54	N.A.	2.48	5.0	2.25	10.3	2.45
Tl^{I}	23	1.59	15	2.24	N.A.	1.61	17	1.64	28.3	1.60	15	1.61
Pb^{II}	3.7	2.33	19	2.24	11	2.68	6.0	2.59	6.4	2.30	10.4	2.56
Bi^{III}	130	2.20	136	2.16	2441	2.37	154	2.38	170	2.17	>5000	—

[a] N.A. = negligible adsorption.

[b] pH of the test solution after ion-exchange.

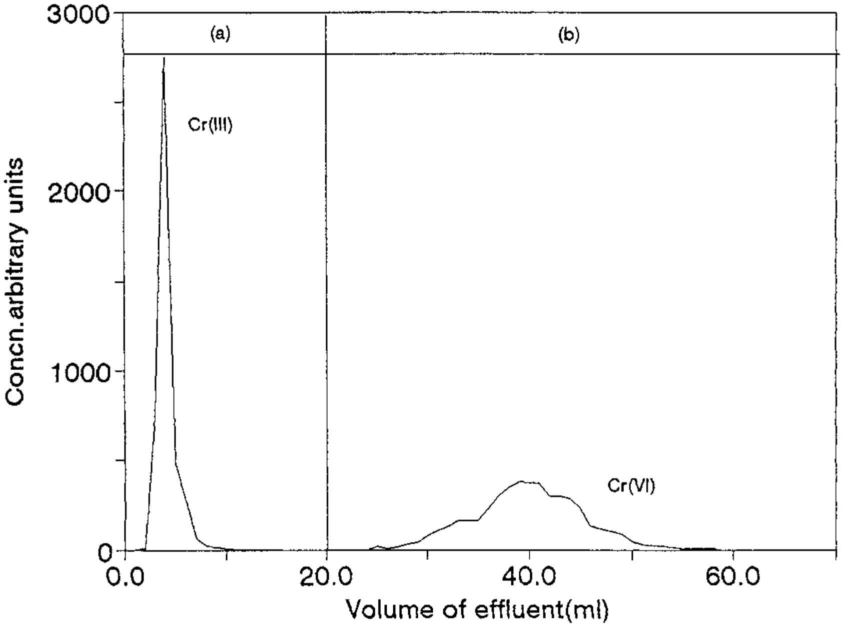

FIG. 4 Elution curve of Cr(III)–Cr(VI). (a) Demineralized water, 0.5 mL/min; (b) 0.25% NH_4OH, 0.5 mL/min. Ion exchanger: 2.0 g CS-4.

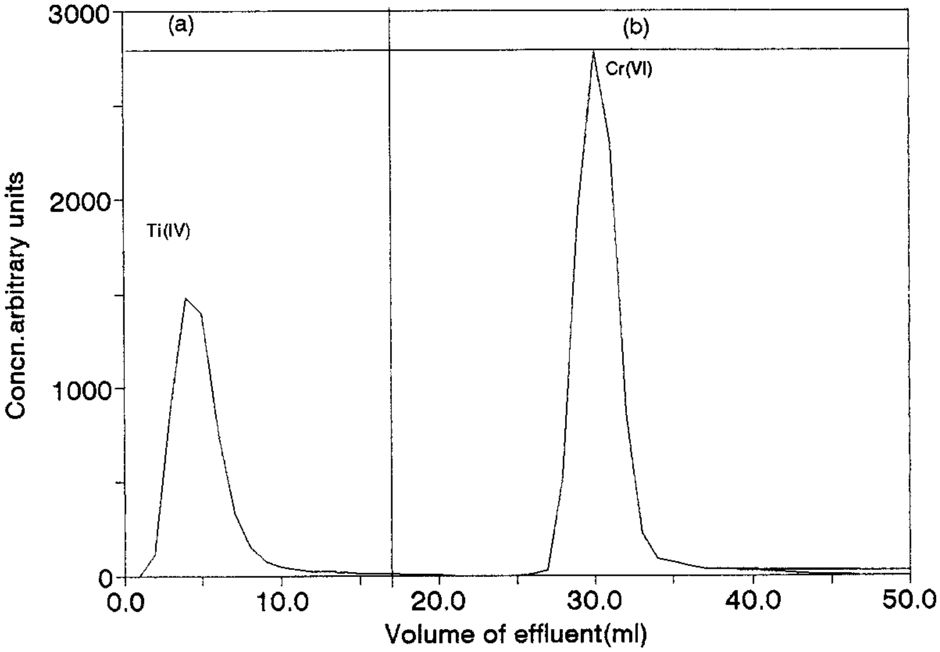

FIG. 5 Elution curve of Ti(IV)–Cr(VI). (a) 0.02 M HNO_3, 0.5 mL/min; (b) 2% NH_4OH, 0.5 mL/min. Ion exchanger: 2.0 g CS-4.

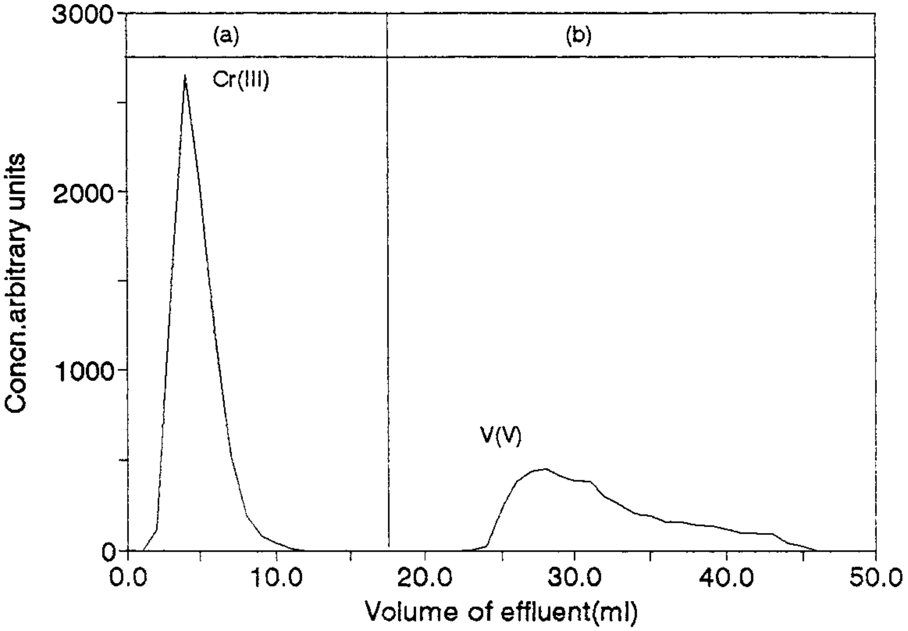

FIG. 6 Elution curve of separation of Cr(III)–V(V). (a) Demineralized water, 0.5 mL/min; (b) 1% NH_4OH, 0.5 mL/min. Ion exchanger; 2.0 g CS-4.

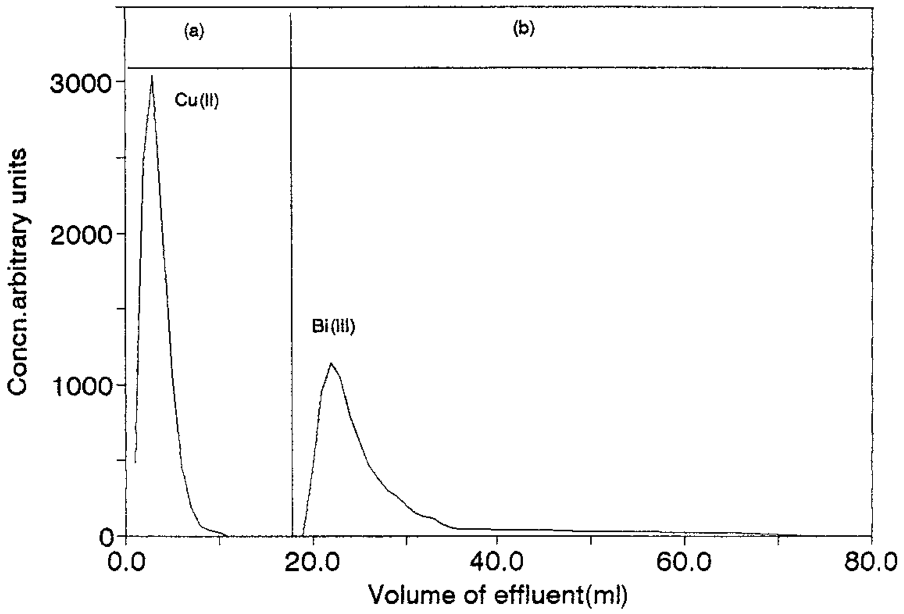

FIG. 7 Elution curve of separation of Cu(II)–Bi(III). (a) Demineralized water, 0.5 mL/min; (b) 0.5 M HNO_3, 0.5 mL/min. Ion exchanger: 1.0 g CS-2.

the column. This is because the cation-exchange nature of this ion exchange is enhanced at a higher pH, thereby releasing the Cr^{VI}. Titanium and vanadium are toxic and form alloys with chromium, which always interferes in their determination and has led to the lack separation methods (22). However, their separations have been accomplished on this ion exchanger (Figs. 5 and 6). Similarly, the rather difficult separation of Cu^{II}–Bi^{III} has also been performed with simple eluents (Fig. 7).

In addition to the nature of this ion exchanger, various factors such as swelling, formation of complexes, nature of the chemical bond, and solvent distribution may be responsible for the wide variation in the distribution coefficient (Table 2) values (23), which offers many possible separations of toxic metal ions from aqueous systems.

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