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NOTE

Quantitative Separations of La(III) from Alkaline Earth Metal Ions Using a New, Poorly Crystalline Inorganic Ion Exchanger: Niobium Molybdate

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During our systematic studies of niobium compounds (*1–4*) as ion-exchange materials, it was found that niobium molybdate has a high thermal stability and can be more easily converted into a poorly crystalline form than the tin (*5*), thorium (*6*), titanium (*7*), and chromium (*8*) molybdates studied in our laboratories. We therefore decided to investigate the ion-exchange behavior of this material. The results are given below.

EXPERIMENTAL

Reagents

Niobium pentoxide (B.D.H., Poole, Great Britain) and sodium molybdate (B.D.H., AR) were used. All other reagents were of Analar grade. Niobium pentoxide was dissolved as earlier (*3*) reported.

Apparatus

The following instruments were used: a Bausch and Lomb Spectronic 20 Colorimeter, an Elico pH meter (model Li–10), a Phillips x-ray unit, a Perkin Elmer Spectrometer Scan microphotograph Phillips unit, Dupont 900 and 950 thermal analyzers, and an electric Sico shaker.

Synthesis of Niobium Molybdate

The samples were prepared by mixing acid solutions of 0.1 *M* niobium sulfate with 0.1 to 1.0 *M* sodium molybdate in various volume ratios. The pH was adjusted over the range 1.0 to 6.0 after mixing by adding ammonia or sodium hydroxide. The precipitates were filtered under suction, washed with demineralized water, and dried at 60°C in an oven. Their ion-exchange capacities were determined by eluting H^+ ions with Na^+ ions. The exchange capacities ranged from 0.60 to 0.90 meq/g. One product was selected for detailed studies. It was made by mixing 0.1 *M* niobium salt with 0.5 *M* sodium molybdate in the volume ratio 1 : 2 and adjusting the pH to 1.0; its capacity was 0.8 meq/g. It was then refluxed in 2 *M* H_2SO_4 for 10 hr and the resulting product was kept in 3 *M* HMO_3 for 3 days.

Composition

Molybdenum (*9*) and niobium (*10*) were determined gravimetrically. The Nb/Mo mole ratio was found to be 0.9346.

Dissolution

To find its chemical stability, 500 mg of material was shaken with 100 mL of the appropriate solution for 6 hr after removal of the undissolved material. Niobium and molybdenum were determined in the filtrate spectrophotometrically (*11*) and gravimetrically (*9*), respectively. The results are shown in Table 1.

Instrumental Studies

X-ray, IR, TGA, and DSC analysis were carried out as earlier (*3*). The results of IR are presented in Table 2.

Determination of Distribution Coefficients

A 250-mg portion of the exchanger (H^+ form) was allowed to stand in 25 mL of cation solution in the appropriate solvent. The mixture was shaken intermittently, and portions of the supernatent liquid were withdrawn and titrated with 0.002 *M* EDTA. The results are shown in Table 3.

Separations

For separation studies a glass column was filled with 500 mg of niobium molybdate in the H^+ form on a glass wool support. The flow rate in all separations was 0.6 to 0.8 mL/min. Alkaline earth metal ions were eluted

TABLE 1

Solubility of Niobium Molybdate

System	Nb (mg/L)	Mo (mg/L)
1. DMW	3.6	20.15
2. 1 *M* NH_4Cl	—	20.90
3. 1 *M* NH_4NO_3	2.8	23.50
4. 4 *M* HNO_3	132.00	418.00
5. 2 *M* H_2SO_4	—	566.20
6. 2 *M* HCl	321	510.20
7. 1 *M* NaOH	Nearly dissolved completely	

TABLE 2

Details of IR Spectrum of Niobium Molybdate, KBr Disk Method

Frequency	Appearance	Designation
3400	Broad	Hydroxo stretching -(O-H)
2940	Sharp	Deformation vibrations of coordinated water
2860	Medium sharp	
1610	Medium broad	Deformation vibrations of interstitial water and hydroxyl groups
1560	Weak broad	Deformation vibrations of M-OH bonds
1360	Very weak	
1120	Very weak	
960	Very weak	Superposition of metal oxygen stretching and aquo wagging twisting and rocking modes
880	Medium weak	

TABLE 3

K_d Values upon NbMo

System/cation	Demineralized water	10^{-2} *M* HNO_3
Mg(II)	26	11
Ca(II)	30	20
Sr(II)	43	22
Ba(II)	20	20
Zn(II)	27	24
Cd(II)	44	16
Hg(II)	0.00	0.00
Cu(II)	>3500	800
Mn(II)	60	60
Al(III)	17	17
Bi(III)	1300	610
La(III)	>3500	620
Pr(III)	>3000	520
Th(IV)	400	500

TABLE 4

Separations Achieved on Niobium Molybdate

System no.	Mixture loaded	Cations eluted	Eluent	Total volume of effluent (mL)	Amount loaded (μg)	Amount found (μg)	% error
1	Mg(II)–La(III)	Mg(II)	A	60	86.4	85.2	−0.93
		La(III)	B	40	194.60	194.60	0.0
2	Ca(II)–La(III)	Ca(II)	A	50	152.00	144.00	−5.26
		La(III)	B	40	194.60	194.60	0.0
3	Sr(II)–La(III)	Sr(II)	A	50	325.60	325.60	0.0
		La(III)	B	40	194.60	189.50	−2.62
4	Ba(II)–La(III)	Ba(II)	A	60	493.20	506.90	+2.77
		La(III)	B	40	194.60	189.50	−2.62

with 0.02 *M* NH_4NO_3, and La(III) was eluted with 0.2 *M* NH_4NO_3. The results are given in Table 4.

RESULTS AND DISCUSSION

The studies on niobium molybdate indicate its fairly reproducible behavior.

The results of tests on chemical dissolution of niobium molybdate are shown in Table 1. The table shows the moderate stability of the material. It is completely dissolved in sodium hydroxide solution, probably due to the formation of sodium niobate and sodium molybdate species. The chemical stability of other molybdates has also been determined, and the sequence in DMW (demineralized water) and in 4 *M* HNO_3 is ThMo (*5*) > NbMo > TiMo (*7*) > CrMo (*8*).

The ion-exchange capacity determinations indicate that the ion exchange takes place with the hydrated form of the cations.

The x-ray diffractogram of niobium molybdate showed broad lines at 6.70, 3.86, 3.37, and 3.18 Å. The poorly crystalline nature has also been observed in electron microphotographs of 190 magnification. No lines were observed in Sn (*5*), Th (*6*), and Ti (*7*) molybdates. Clearfield et al. (*12*) synthesized crystalline ZrMo and characterized its crystal structure. De et al. (*13*) synthesized amorphous cerium molybdate. The present study may therefore lead to the crystallization of niobium molybdate.

The results of thermogravimetric analysis are presented in Fig. 1, from which it can be seen that the niobium molybdate is more thermally stable than CrMo (*8*), NbSb (*3*), and NbAs (*1*) in the temperature range of 50 to 500°C. The thermal stability sequence regarding weight loss is NbMo > NbSb (*3*) > NbAs (*1*) > CrMo (*8*).

The weight loss in NbMo is highest between 100 and 200°C. It may be due to the removal of water of crystallization as well as coordinated water. The weight loss observed between 250 and 400°C is probably due to the conversion of molybdic acid to its oxides and condensation of its hydroxyl groups.

Differential scanning calorimetric analysis also indicates that the material is fairly stable up to 350°C.

The ion-exchange capacity of molybdates of Cr (*8*), Sn (*5*), Ti (*7*), and Th (*6*) becomes negligible just above 100°C. The ion-exchange capacity of NbMo is at a maximum in the temperature range of 40 to 400°C, i.e., NbMo > SnMo (*5*) > TiMo (*7*) > CrMo (*8*) > ThMo (*6*), and this is the most useful range for analytical work.

This exchanger can therefore be used as an ion exchanger up to 300°C. This stability may be due to the inertness of niobium oxide.

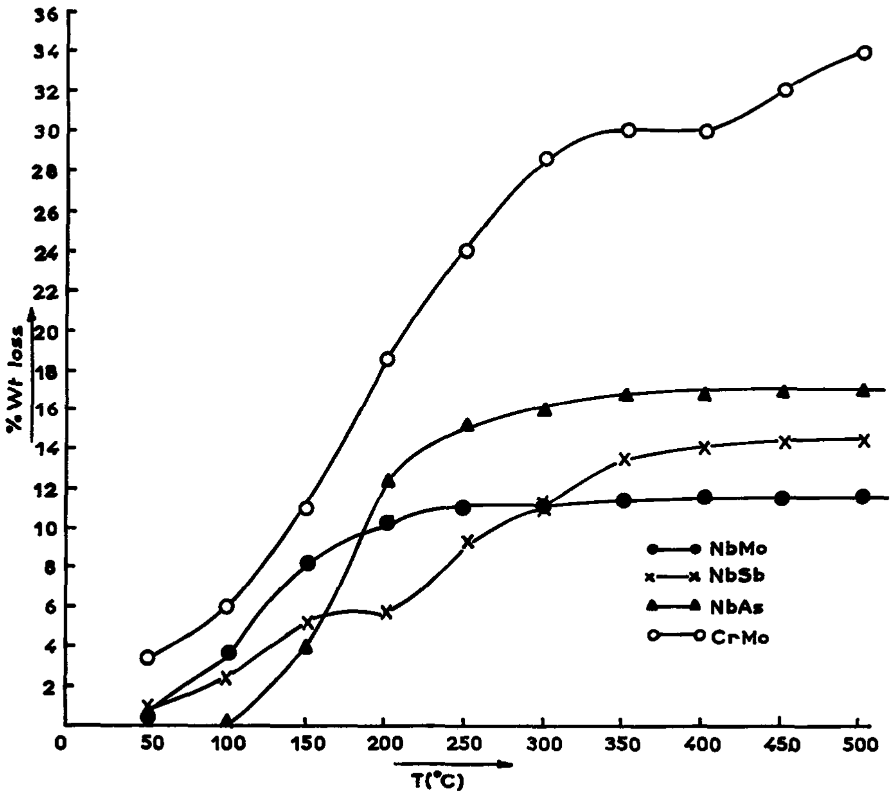

FIG. 1. Thermogravimetric analysis curves of inorganic ion exchangers.

The distribution coefficients of 14 metal ions have been determined in demineralized water and 10^{-2} M HNO_3 (pH = 2). The K_d values are small in a nitric acid medium than in water. Hg(II) shows no adsorption on the material. Niobium molybdate shows high adsorption toward Cu(II), Bi(III), La(III), Pr(III), and Th(IV), but low adsorption for alkaline earth metal ions, Zn(II), Cd(II), Mn(II), and Al(III).

This study suggests that niobium molybdate may be specific for La(III) and Pr(III) which may be separated from numerous metal ions. Thus the K_d value of La(III) is much greater than those of Mg(II), Ca(II), Sr(II), and Ba(II). Alkaline earth metal ions have therefore been separated from La(III) quantitatively. These are eluted with 2×10^{-2} M NH_4NO_3 while La(III) is eluted with 2×10^{-1} M NH_4NO_3. The results of the separations are shown in Table 4.

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