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Studies on Inorganic Ion Exchangers. Part VI. Synthesis and Physicochemical Properties of Cerium(IV) Molybdate Ion-Exchanger and Some Selective Ion-Exchange Separations

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NOTE

Studies on Inorganic Ion Exchangers. Part VI. Synthesis and Physicochemical Properties of Cerium(IV) Molybdate Ion-Exchanger and Some Selective Ion-Exchange Separations

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Abstract

Cerium (IV) molybdate has been prepared under various conditions. Its properties and ion exchange behavior have been investigated. Separations of Mg^{2+}, Zn^{2+}, Co^{2+}, and Cu^{2+} from Pb^{2+} have been achieved.

During the last two decades remarkable interest has grown in synthetic inorganic ion exchangers (*1*). Quite a large number of insoluble acid salts have been investigated as ion exchangers. Various compounds of cerium(IV), viz., phosphate (*2–5*), arsenate (*6*), antimonate (*7*), and tungstate (*8*) have been studied. Work on thorium phosphate and thorium tungstate ion exchangers has already been reported (*9–13*) from this laboratory. These studies are now extended to cerium(IV) molybdate about which information is lacking in the literature.

The present communication describes the preparation, properties, and ion-exchange behavior of cerium(IV) molybdate and some selective ion-exchange separations from Pb^{2+} on a cerium(IV) molybdate column.

EXPERIMENTAL

Reagents. All the chemicals used were of analytical reagent grade (B.D.H. or E. Merck).

Apparatus: pH measurements were made with an Elico Model 10 pH meter, Hyderabad (India). For spectrophotometric work Spectromom 202 (Hungary) was used.

Preparation of Cerium(IV) Molybdate

Cerium(IV) molybdate of different compositions was prepared by mixing ceric sulfate solution and ammonium molybdate or sodium molybdate solutions on a steam bath. The precipitates were filtered and washed with deionized water up to pH 4 and dried over P_2O_5. Details are given in Table 1.

RESULTS AND DISCUSSION

Composition of Cerium(IV) Molybdate

About 0.3 g of the sample was weighed accurately and dissolved in 50 ml H_2SO_4 (1:4). Cerium(IV) hydroxide was precipitated by the addition of 10% NaOH, filtered, and washed with 1% NaOH. The filtrate was kept reserved for estimation of molybdenum. The precipitate was dissolved in minimum volume of H_2SO_4 (1:4) and then titrated by standard Mohr

TABLE 1

Preparation, Composition, and Probable Formula of Cerium(IV) Molybdate

Batch no.	Volume of 0.1 *M* $Ce(SO_4)_2$ in 1.0 *N* H_2SO_4: volume 0.1 *M* ammonium or sodium molybdate[a]	Digestion time (hr)	Composition		Probable formula
			Mo: Ce	Ce: H_2O	
1	3:2	12	4.1	1:4	$Ce(HMoO_4)_4 \cdot 2H_2O$
2	1:1	12	8.29	1:6.1	$Ce(HMo_2O_7)_4 \cdot 4H_2O$
3	1:4	6	2.33	1:3	$Ce(OH)_6[Mo_7O_{24}] \cdot 6H_2O$

[a] Ammonium molybdate was used for Batch nos. 1 and 2; sodium molybdate was used for Batch no. 3.

salt using ferroin as an indicator (*14*). Molybdenum was estimated gravimetrically by oxine (*14*). Details of the composition are given in Table 1.

Chemical Stability

The chemical stability of the exchanger toward mineral acids, water, and ammonium hydroxide has been studied. Sample no. 3 was shaken with dilute H_2SO_4, $HClO_4$, water, and ammonium hydroxide for 12 hr at room temperature. The sample was also refluxed with dilute H_2SO_4. Solubilities of cerium (*15*) and molybdenum (*16*) were determined spectrophotometrically. The sample is fairly stable in water, 0.1 N H_2SO_4, 0.1 N $HClO_4$, and 1.0 N $HClO_4$.

Heat Treatment

One gram of the sample was taken in a silica crucible and heated for 1 hr from 100 °C in steps of 100 °C. At 100 °C it was heated in an air oven and from 200 to 700 °C in a muffle furnace. The weight loss curve is given in Fig. 4. On the basis of weight loss, the probable formula, which is shown in Table 1, has been calculated using the equation of Alberti et al. (*17*).

pH Titration Curves

The Topp and Peppers (*18*) method was employed for the pH titration curve. 50 ml of different alkalies MOH (M = Li, Na, or K) containing different amounts was added to 1 g of the exchanger. After shaking intermittently for 2 days, the pH was noted. The pH titration curves are given in Figs. 1 and 2.

Ion Exchange Capacity

The ion-exchange capacity was determined by shaking intermittently 1 g of the exchanger with 50 ml of 1.0 M Na_2SO_4 or 0.5 M K_2SO_4 at pH 6 to 6.5. The hydrogen ion liberated was estimated by titrating a 10-ml aliquot with a standard NaOH solution using methyl orange indicator. The results are given in Table 2. The loss in exchange capacity of the sample on heating at different temperatures has been determined. The results, as shown in Table 3, indicate that exchange capacity is virtually lost at 300 °C.

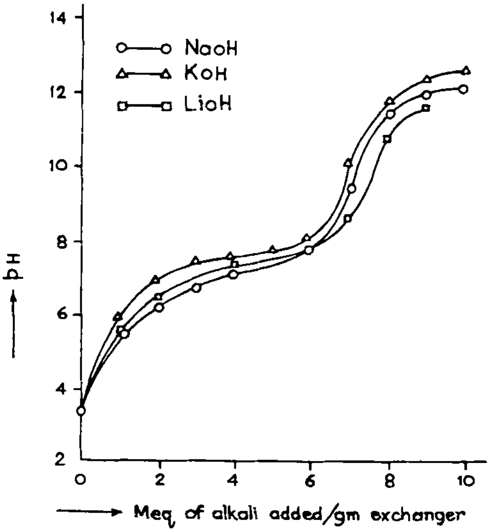

FIG. 1. pH titration curve for cerium(IV) molybdate (Batch No. 3)

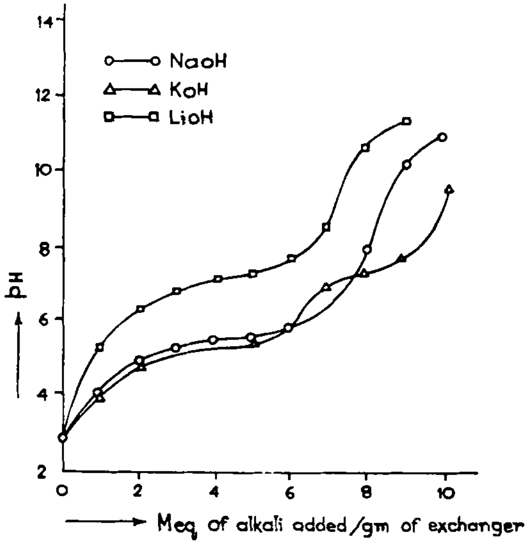

FIG. 2. pH titration curve for cerium(IV) molybdate (Batch No. 2)

TABLE 2

Exchange Capacity of Cerium(IV) molybdate

	Ion exchange capacity (meq/g)		
Metal ion	Sample no. 1	Sample no. 2	Sample no. 3
Na^+	0.21	0.25	0.26
K^+	0.39	0.37	0.32

TABLE 3

Exchange Capacity at Different Temperatures

	Exchange capacity (meq/g)		
Temp (°C)	Sample no. 1	Sample no. 2	Sample no. 3
100	0.20	0.23	0.24
200	0.16	0.14	0.19
300	0.09	0.06	0.09

Column Elution of Hydrogen Ion

A tube of 1.1 cm i.d. was fitted with 1 g of the exchanger (Sample no. 3) supported at the bottom by glass wool. Hydrogen ion was eluted with 1.0 *M* Na_2SO_4 and 0.1 *M* Na_2SO_4. Each successive 5 ml of eluent was titrated with standard NaOH using methyl orange as indicator. Elution curves (Fig. 3) show that all the hydrogen ion is practically completely eluted with 1.0 *M* Na_2SO_4 after passing 40 ml of eluent. The pH of the eluent was maintained at 6 to 6.5.

Distribution Coefficient (K_d)

Distribution coefficients of metal ions were determined as in the earlier paper (*10*). The concentration of metal ion was adjusted to 2×10^{-4} *M*. As bismuth, lead, cadmium, strontium, thorium, and barium were completely absorbed at that concentration, higher concentration was employed for these ions. The initial pH of these ions was adjusted to 2.0. These ions were estimated by using 2×10^{-3} *M* EDTA solution (*19*). A 10-ml aliquot was taken out of 50 ml of solution, and the results are summarized in Table 4.

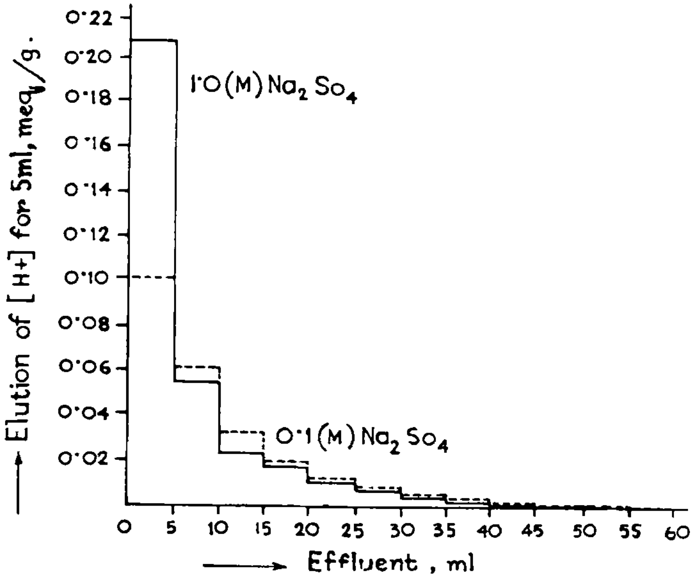

FIG. 3. Elution curve of hydrogen ion.

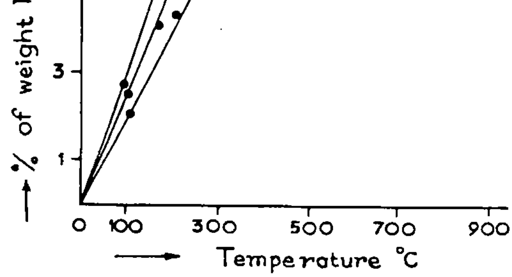

FIG. 4. Percent weight loss curve for cerium molybdate as a function of temperature.

TABLE 4

Distribution Coefficients for Metal Ions on Cerium(IV) Molybdate

Metal ion	K_d (ml/g)	Metal ion	K_d (ml/g)
Cu^{2+}	4.88	Co^{2+}	4.99
Zn^{2+}	1.61	Al^{3+}	0.00
Mg^{2+}	1.15	Mn^{2+}	8.34
Ca^{2+}	17.02	Sr^{2+}	94.12
Ba^{2+}	459.1	Ni^{2+}	8.34
Pb^{2+}	788.1	Bi^{3+}	T.A.[a]
Hg^{2+}	2.26	Th^{4+}	T.A.[a]
Cd^{2+}	113.4		

T.A. = Total absorption.

TABLE 5

Separation of Lead from Other Metals on Cerium(IV) Molybdate Column

No.	Mixture separated	Eluents	Effluent (ml)	Taken (mg)	Found (mg)	Error (%)
1	Zn^{2+}	0.1% $NaNO_3$(pH 2)[a]	70	0.14	0.14	0.0
	Pb^{2+}	2 *M* $NaNO_3$ in 0.15 *M* HNO_3	40	0.47	0.48	+2.1
2	Mg^{2+}	1% $NaNO_3$ (pH 2)[a]	50	0.060	0.059	−1.6
	Pb^{2+}	2 *M* $NaNO_3$ in 0.15 *M* HNO_3	50	0.47	0.48	+2.1
3	Co^{2+}	0.25% $NaNO_3$ (pH 2)[a]	55	0.11	0.10	−9.8
	Pb^{2+}	2 *M* $NaNO_3$ in 0.15 *M* HNO_3	42.5	0.47	0.48	+2.1
4	Cu^{2+}	1% $NaNO_3$ (pH 2)[a]	30	0.11	0.11	0.0
	Pb^{2+}	2 *M* $NaNO_3$ in 0.15 *M* HNO_3	20	0.47	0.49	+4.0

[a] pH was adjusted with HNO_3.

Ion Exchange Separations

Binary separation of Pb^{2+} from Cu^{2+}, Co^{2+}, Zn^{2+}, and Mg^{2+} has been achieved by using a column containing about 5 g of the exchanger (Sample no. 2). Before filling the column, the exchanger was placed in a beaker and washed with water (pH 2 adjusted with HNO_3) until it was free from all turbidity to facilitate easy flow of the solution through the exchanger column. Then the column was washed with 1.0 *N* H_2SO_4 and water. Some typical plots of the elution curve for the metal ions from lead are shown in Fig. 5.

It is evident from studies of the distribution coefficient of metal ions on cerium(IV) molybdate that some selective ion-exchange separations of lead from other metals are feasible. Thus separations of copper, zinc, mag-

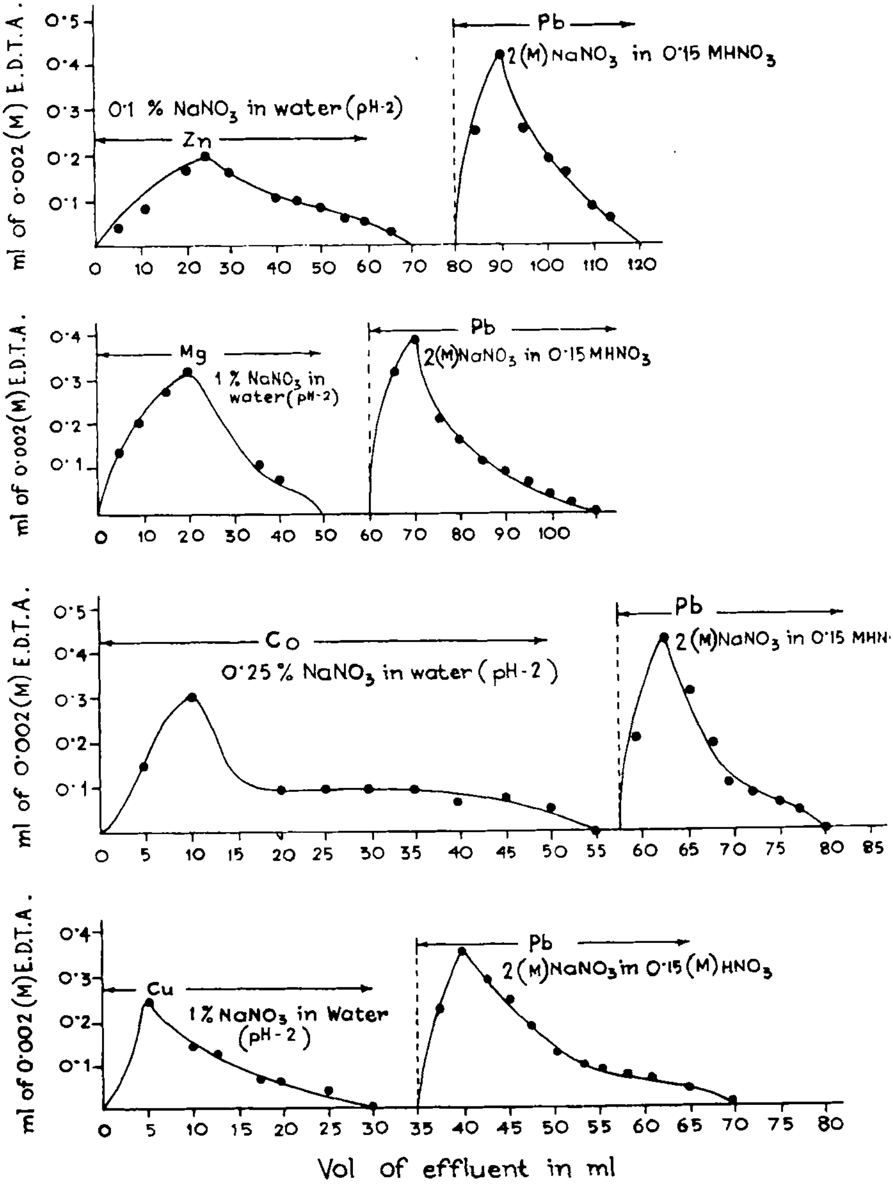

FIG. 5. Separation curve for cerium molybdate separation of metal ions on cerium(IV) molybdate column (Batch No. 2).

nesium, and cobalt from lead have been achieved. The separations were carried out at pH 2. Distribution studies could not be performed at higher pH values because the solution tends to be colloidal (Table 5).

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