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Studies on Synthetic Inorganic Ion Exchangers. VI. Synthesis and Characterization of Iron(III) Molybdate as an Ion Exchanger

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Six preparations of iron(III) molybdate were obtained at various pH values under different conditions. They all possess cation exchange properties. The preparation, obtained by reaction of iron(III) nitrate with ammonium molybdate at pH 1 with 24 h refluxing, is the stablest and has an ion exchange capacity of 1.39 mequiv. g^{-1}. The mole ratio of Fe: Mo is 1: 3. Distribution coefficients for many metal ions were determined on this preparation. On the basis of pH titrations, chemical and thermal analyses, and infrared and Mössbauer spectra, a tentative structure of iron(III) molybdate is proposed.

Since the classical work of Amphlett[1] numerous inorganic ion exchangers have been prepared and used for several possible applications.[2—5] Recently, some studies on iron-based exchangers have been reported.[6—8] A search of literature showed that no studies have so far been reported on iron(III) molybdate. In the present report we summarize synthesis and ion-exchange and physicochemical properties of iron(III) molybdate as a new ion exchanger.

Experimental

Reagents. Iron(III) nitrate (B. D. H.) and ammonium molybdate (Reanal, Hungary) were used for the synthesis. All other materials used were of analytical grade.

Apparatus. A thermostated oven, digital pH meter, TGA instrument (Fertilizer Corp. of India, Sindhri), Spectrochem 2000 (Hungary), Specol Spectrophotometer, MBS-35 (ECIL) Mössbauer apparatus were used for drying samples, pH measurements, thermal analysis, infrared and visible spectrophotometric measurements, and Mössbauer studies, respectively.

Synthesis. Six samples of iron(III) molybdate were prepared by mixing 0.05 mol dm^{-3} solution of iron(III) nitrate with 0.05 mol dm^{-3} solution of ammonium molybdate under the conditions given in Table 1. The pH of the mixed solution was adjusted by adding either acid or alkali solution. The precipitate obtained was filtered and washed with demineralized water. The gel was dried at 40 °C. The dried product broke down into granules when immersed in water. The material was converted into the hydrogen form by treating with 0.1 mol dm^{-3} nitric acid for 24 h with occasional shaking and intermittent supply of the acid. The material was then washed free of acid with demineralized water and was finally dried at 40 °C.

Ion-exchange Capacity. The ion-exchange capacity of a sample of iron(III) molybdate was determined by taking 1.0 g of the H-form exchanger in a glass column having a glass wool support. The column after being washed with demineralized water was eluted with 1.0 mol dm^{-3} sodium nitrate solution. A 400 cm^3 portion of the effluent was collected at a rate of 15—20 drops/min. The H^+ concentration of the effluent was determined by titration with a standard sodium hydroxide solution.

Ion-exchange capacity for some uni- and bivalent cations on sample 6 (Table 1) was also determined.

Chemical Analysis. One-half gram of sample was treated with 5 cm^3 of each of nitric and hydrochloric acids until it was dissolved, and diluted with water. Iron(III) was precipitated as iron(III) hydroxide and estimated. The molybdenum in the filtrate was precipitated by 8-quinolinol and determined as $MoO_2(C_9H_6ON)_2$.

Chemical Stability. Exchanger samples (0.2 g) were kept separately for 24 h in 20 cm^3 of each of various solvents, such as nitric, oxalic, hydrochloric, and acetic acids, dimethylformamide, and dioxane, and then filtered. The iron and molybdenum in the filtrate were determined spectrophotometrically by the 1,10-phenanthroline and thiocyanate methods, respectively.

pH Titration. pH titration on 0.2 g of iron(III) molybdate was performed by using 0.1 mol dm^{-3} standard solutions of lithium, sodium, and potassium hydroxides, aqueous ammonia, and their respective salts according to the method of Topp and Pepper.[9] The volume ratio of alkali to its salt solution was selected in such a way that the total volume of 20 cm^3 was to be maintained in each conical flask.

Sorption Studies. Distribution Coefficients of nineteen metal ions were determined on iron(III) molybdate in 50% ethanol. The loading of metal ions for the system was less than 3% of the working ion-exchange capacity of sample after 24 h of equilibrating period. The equation used for the calculation is,

TABLE 1. CONDITIONS OF PREPARATION AND PROPERTIES OF IRON(III) MOLYBDATES

	Conditions of synthesis				Properties					
Sample	Molarity of reagents mixed		Mixing ratio	pH	Refluxing time/h	Color in H-form	Ion exchange capacity for Na^+/mequiv. g^{-1}	Composition	Solubility in water/μg in 20 cm^{-3}	
	Fe	Mo	Fe:Me					Fe:Mo	Fe	Mo
1	0.05	0.05	2:1	1.0	—	Yellow	3.80	1:3.5	320	500
2	0.05	0.05	2:1	2.0	—	Brown	1.56	1:4.0	280	850
3	0.05	0.05	3:1	1.0	—	Yellow	3.43	1:3.8	420	600
4	0.05	0.05	2:1	1.0	8	Yellow	1.55	1:3.2	220	720
5	0.05	0.05	2:1	1.0	12	Yellow	1.52	1:3.1	240	520
6	0.05	0.05	2:1	1.0	24	Yellow	1.39	1:3.0	150	360

Table 2. Ion exchange capacity of iron(III) molybdate sample 6

Metal ion	Salt used	Solution	Hydrated radii/Å	pH	Ion exchange capacity/mequiv. g^{-1}
Li^+	$LiNO_3$	(1.0 mol dm^{-3})	3.40	6.05	1.34
Na^+	NaCl	(1.0 mol dm^{-3})	2.76	5.50	1.39
K^+	KNO_3	(1.0 mol dm^{-3})	2.32	6.90	1.47
Mg^{2+}	$Mg(NO_3)_2$	(0.5 mol dm^{-3})	7.00	6.00	1.80
Ca^{2+}	$Ca(NO_3)_2$	(0.5 mol dm^{-3})	6.30	6.40	1.86
Sr^{2+}	$Sr(NO_3)_2$	(0.5 mol dm^{-3})	—	6.50	1.92

$$K_d/\text{cm}^3\,\text{g}^{-1} = \frac{I-F}{F}\times\frac{20}{0.2},$$

where I and F are the volumes of the 0.025 mol dm^{-3} EDTA solutions required for titration before and after the equilibration, respectively. The total volume of the equilibrating solution was 20 cm^3 and the amount of exchanger taken was 0.2 g.

Structural Studies. Infrared absorption spectra of iron(III) molybdate in an H-form exchanger dried at 40, 100, 200, 600, or 700 °C were obtained in KBr media.

Thermogravimetric analysis of iron(III) molybdate in H-form exchanger was performed at a heating rate of 10 °C min^{-1}.

Mössbauer spectra of iron(III) molybdate in H-form exchanger dried at 40, 200, or 500 °C were obtained by using a ^{57}Co source at a constant acceleration. Sodium pentacyanonitrosyl ferrate(III) was used as the reference for the value of isomer shift to be reported.

Results and Discussion

Ion-exchange capacities of various samples prepared by refluxing are comparatively low. This is associated with the fact that stabler materials were obtained by refluxing the mother liquor. In order to investigate the working capacity of the exchanger, capacities for some uni- and bivalent cations were determined (Table 2). In general, exchange capacities for uni- and bivalent ions are found to be in the orders: $K^+>Na^+>Li^+$ and $Sr^{2+}>Ca^{2+}>Mg^{2+}$. These results show that ion exchange capacity depends upon hydrated radii of metal ions of the same group. We used the equilibrium in the solution phase where hydrated radii play an important role, so that the ion exchange capacity in the same group is found to decrease as the (hydrated) radii of ingoing cations increase.

A Chemical analysis of various samples (Table 1) revealed that Fe:Mo is 1:3. The results in Table 1 show that sample 6 is the stablest among the six samples. Its solubility in most of the common solvents is quite low as seen from Table 3. It is also observed that the chemical stability increases with increasing refluxing time. The pH titrations performed (Fig. 1) show that iron(III) molybdate behaves as a weak bifunctional cation exchanger.

Table 3. Solubility of iron(III) molybdate sample 6 in various solvents

Solvent		Solubility/μg in 20 cm^3	
		Fe	Mo
HNO_3	(1.0 mol dm^{-3})	460	288
$H_2C_2O_4$	(1.0 mol dm^{-3})	1540	1220
HCl	(1.0 mol dm^{-3})	720	284
CH_3COOH	(1.0 mol dm^{-3})	1500	450
DMF		0	60
Dioxane		0	40

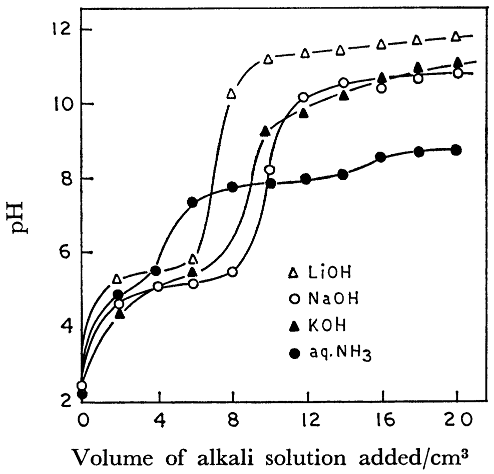


Fig. 1. pH titrations of iron (III) molybdate by added salt method.

Table 4. Isomer shift and quardrupole splitting of various inorganic iron compounds

Compound	Drying temp/°C	δ/mm s^{-1}	ε/mm s^{-1}
Iron(III) molybdate	R.T.[a]	0.68	0.48
Iron(III) molybdate	200	0.61	0.59
Iron(III) molybdate	500	0.64	0.00
α-FeOOH	R.T.	0.53	0.00
β-FeOOH	R.T.	0.43	0.62
γ-FeOOH	R.T.	0.48	0.54
δ-FeOOH	R.T.	0.45	0.00

a) R.T.: Room temperature.

Results of Mössbauer studies are given in Table 4. Originally, it was thought that one of the fundamental requirements of the Mössbauer effect expected to become actually applicable would be that Mössbauer atoms should be bound in a crystal lattice. It was, however, shown in an earlier paper[10)] that there is a high possibility of observing the effect in amorphous substances (or in solid solution).

The Mössbauer spectrum of iron(III) molybdate in the H-form exchanger dried at 40 °C consists of a sharp and well defined doublet with δ=0.68 mm/s and

$\varepsilon = 0.48$ mm/s at room temperature. These parameters characterize an iron atom in the "high spin tetravalent" state incorporated in the distorted octahedral site in the gel structure. The room temperature spectrum of the iron(III) molybdate dried at 200 °C shows a doublet which indicates a more covalent bonding and less distorted sites. Further, raising the drying temperature to 500 °C gives an unresolved single broad peak indicating a motional narrowing magnetic spectrum at room temperature. Further heat treatment results in growth of small particles in large crystallites as indicated by the isomer shift.

The results given in Table 4 allow a comparison of Mössbauer parameters of iron(III) molybdate dried at 40 °C with those of α,β,γ, and δ-FeOOH, which rules out the existence of α- and δ-FeOOH in the condensed phase with molybdate on the basis of quadrupole splitting. The value of quadrupole splitting for iron(III) molybdate which is close to that for γ-FeOOH, indicates the presence of the latter in the former. The product dried at 200 °C contains β-FeOOH, whereas the product dried at 500 °C contains iron in the form of α-Fe_2O_3.

The infrared spectra of the samples dried at 100, 200, 600, and 700 °C show that, as the drying temperature is raised, intensities of the bands at 3300 and 1625 cm^{-1} are decreased and ultimately caused to disappear at 600 °C due to complete removal of the water and OH groups present in the ion exchanger. Hence the product dried at 700 °C is simply a mixed oxide of iron and molybdenum, as confirmed by a single infrared band at 850 cm^{-1} due to the metal-oxygen bond.

In the light of the above discussion, chemical analysis, pH titrations, thermal analysis, Mössbauer spectra, and infrared absorption studies, a tentative structure of iron(III) molybdate can be worked out.

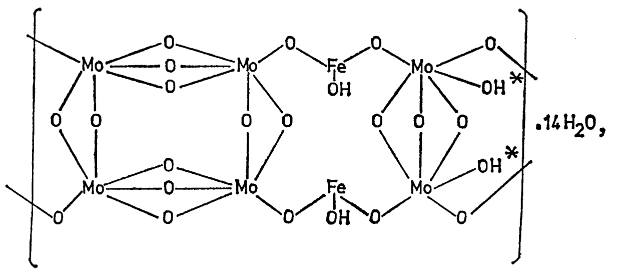
Results of the chemical analysis show that the ratio Fe:Mo in sample 6 iron(III) molybdate is 1 : 3. The thermogravimetric analysis shows that the loss in weight due to water molecules amounts to an extent of 20%. Since on heating oxides of iron and molybdenum are formed in the same ratio, the empirical formula for the mixed oxide should be $Fe_2O_3 \cdot 6MoO_3$ with a formula weight 1023.

If n is the number of moles of water per mole of mixed oxide, then

$$\frac{1800n}{(1023+18n)} = 20 \text{ or } n=24,$$

and the formula weight is 1275.

Thus, the structure of iron(III) molybdate may be



where the asterisked hydrogens are exchangeable protons.

Iron(III) molybdate acts selectively for Pb^{2+}, Co^{2+}, Sr^{2+}, Hg^{2+}, and Bi^{3+}. For many other cations K_d values are quite low, as shown in Table 5. This makes it possible to separate the above cations from a number of other cations.

Table 5. Distribution coefficients (K_d) for cations on iron(III) molybdate

Cation	K_d/cm^3 g^{-1}	Cation	K_d/cm^3 g^{-1}
Mg^{2+}	21	Ni^{2+}	17
Zn^{2+}	21	Cd^{2+}	20
Ba^{2+}	50	Bi^{3+}	400
Sr^{2+}	316	Al^{3+}	45
Ca^{2+}	80	La^{3+}	12
Pb^{2+}	650	Nd^{3+}	29
Cu^{2+}	15	Th^{4+}	80
Mn^{2+}	9	V^{5+}	121
Hg^{2+}	155	Ce^{4+}	54
Co^{2+}	239		

Table 6. Separation factors of some pairs of cations on iron-based synthetic inorganic ion exchanges

Separaction factor	Iron(III) molybdate	Iron(III) antimonate	Iron(III) phosphate
α^{Zn}_{Pb}	30.4	8.2	10.5
α^{Ba}_{Pb}	13.0	2.0	6.3
α^{La}_{Pb}	56.6	0.0	—
α^{Cu}_{Pb}	42.2	0.0	7.8
α^{Ni}_{Pb}	36.9	1.2	5.7
α^{Hg}_{Sr}	15.3	1.4	—
α^{Mn}_{Sr}	33.6	2.9	1.9
α^{Cd}_{Sr}	15.8	0.6	—

The order of selectivity for various cations is found to be: $Pb^{2+} > Bi^{3+} > Sr^{2+} > Co^{2+} > Hg^{2+} > V^{5+} > Th^{4+} = Ca^{2+} > Ce^{4+} > Ba^{2+} > Al^{3+} > Nd^{3+} > Zn^{2+} = Mg^{2+} = Cd^{2+} > Ni^{2+} > Cu^{2+} = La^{3+} > Mn^{2+}$.

On the basis of the selectivity sequence, separation factors were calculated (Table 6), and in all the cases separation factors on iron(III) molybdate are found to be greater than the other iron-based ion exchangers.

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