Synthesis and Ion Exchange Properties of Magnesium Molybdosilicate as Dependent on the Ionic Potential of the Exchanging Ions

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Magnesium molybdosilicate was synthesized and its ion exchange properties were investigated towards certain metal ammine complexes namely Cu(II), Zn(II), Cd(II), Ni(II) and Co(II) by a batch equilibration technique as a function of pH, concentration and steric characteristics of the exchanging ions.

Key words: Magnesium molybdosilicate, Ion exchange, Metal ammine complexes.

INTRODUCTION

During the last 10–15 years, inorganic ion exchangers have firmly occupied their position among the ion exchange materials[1]. The salts of heteropolyacids are one class of such compounds[2]. The molybdosilicates of this class are of key importance in the functioning of certain enzymes apart from many uses in analytical chemistry[3]. Magnesium molybdosilicate as ion exchanger has not been explored much as indicated by literature survey. The present study explores some of its ion exchange properties. The study focuses its attention on the effect of pH, concentration and steric properties (ionic potential) of the exchanging ions on the exchange behaviour of the synthesized material.

EXPERIMENTAL

All the chemicals used were of AR grade. Demineralized water was used throughout the work. All the experimental observations were done at room temperature (30 ± 5°C).

Synthesis of the ion exchanger

Magnesium molybdosilicate was prepared by mixing the aqueous solutions of magnesium sulphate, ammonium molybdate and sodium metasilicate in the mole ratio of 7 : 1 : 4, respectively with constant stirring. Additions of the solutions were in the following order: sodium metasilicate, ammonium molybdate, then magnesium sulphate. The pH of the mixture was adjusted to 10 with 1 : 1 ammonia. Gel-like precipitates were left for 24 h, filtered, washed with demineralized water 3–4 times and dried at 50°C and then sieved. Its ion exchange behaviour was confirmed by pH-metric titrations[4].

Prepration of metal ion solutions and ammine complexes

Stock solutions of Cu(II), Zn(II), Cd(II), Ni(II) and Co(II) metal ions of concentration 0.4 M were prepared by dissolving the requisite quantities of AR

grade metal sulphate in demineralized water. Ammine complexes of the metals of different ionic strengths were obtained by taking appropriate volumes of the stock solutions, adding ammonia solution and adjusting their pH with dilute ammonia (1 : 2) and dilute acetic acid (1 : 2) solution. All the pH measurements were carried out with the help of Systronics pH-meter 335 in conjunction with an Elico glass electrode.

Sorption of metal ammines as a function of pH and concentration

The metal ammine uptake was studied by batch operation[5] in which 25 mL of the metal ammine solution of specified concentration and pH was shaken for 1 h in a stoppered conical flask with 250 mg of the magnesium molybdosilicate by a mechanical shaker (wrist action with speed controlling device). After equilibration, concentration of the metal ion in the clear supernatant was determined complexometrically[6] with EDTA solution using eriochrome black-T as indicator [for Zn(II) and Cd(II)], using murexide as indicator [for Co(II) and Ni(II)] and iodometrically[7] for Cu(II).

Knowing the initial and equilibrium concentration of the metal ion in the external solution, the amount taken up by the exchanger (q_A) was calculated. K_d values (distribution coefficient) were calculated using the following relation:

$$K_d = \frac{100 - X}{X} \cdot \frac{V}{m}$$

where K_d = distribution coefficient ; X = percentage of ion remaining in solution; V = volume of solution in mL and m = quantity of the exchanger in g.

Effect of pH and concentration on the uptake of metal ammines is summarized in Tables 1–3.

TABLE-1
CONCENTRATION OF THE EXCHANGING ION SOLUTION = 0.01 M,
AMOUNT OF THE EXCHANGER USED EVERY TIME = 250 mg

pH	q_A (meq)					$K_d \times 10^2$				
	Cu^{2+}	Zn^{2+}	Cd^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Ni^{2+}	Co^{2+}
8.0	0.150	0.122	0.111	0.065	0.090	1.500	0.953	0.798	0.351	0.562
8.5	0.172	0.148	0.135	0.092	0.112	2.205	1.451	1.174	0.582	0.811
9.0	0.193	0.162	0.151	0.110	0.125	3.386	1.841	1.525	0.786	1.000
9.5	0.205	0.175	0.161	0.122	0.136	4.555	2.333	1.809	0.953	1.193
10.0	0.202	0.189	0.168	0.127	0.147	4.208	3.098	2.049	1.032	1.427
10.5	0.197	0.178	0.172	0.139	0.155	3.717	2.472	2.205	1.252	1.631
11.0	0.187	0.170	0.157	0.120	0.142	2.968	2.125	1.688	0.923	1.315

TABLE-2

CONCENTRATION OF THE EXCHANGING ION SOLUTION = 0.10 M,
AMOUNT OF THE EXCHANGER USED EVERY TIME = 250 mg

pH	q_A (meq)					$K_d \times 10^2$				
	Cu^{2+}	Zn^{2+}	Cd^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Ni^{2+}	Co^{2+}
8.0	0.431	0.395	0.341	0.240	0.290	0.208	0.188	0.158	0.106	0.131
8.5	0.447	0.420	0.355	0.251	0.315	0.218	0.202	0.165	0.112	0.144
9.0	0.475	0.446	0.378	0.267	0.372	0.234	0.217	0.176	0.119	0.150
9.5	0.494	0.455	0.380	0.275	0.332	0.246	0.222	0.179	0.123	0.153
10.0	0.485	0.465	0.385	0.287	0.335	0.241	0.228	0.182	0.130	0.155
10.5	0.469	0.450	0.397	0.300	0.344	0.231	0.219	0.189	0.136	0.159
11.0	0.448	0.430	0.382	0.285	0.325	0.218	0.208	0.180	0.129	0.149

TABLE-3

pH OF VARIOUS EXCHANGING ION SOLUTIONS:
Cu^{2+} (9.5), Zn^{2+} (10), Cd^{2+} (10.5), Ni^{2+} (10.5), Co^{2+} (10.5)

Initial conc. (mol L^{-1})	q_A (meq)					$K_d \times 10^2$				
	Cu^{2+}	Zn^{2+}	Cd^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Ni^{2+}	Co^{2+}
0.01	0.205	0.189	0.172	0.139	0.155	4.555	3.098	2.205	1.252	1.631
0.02	0.227	0.224	0.202	0.156	0.188	0.831	0.811	0.678	0.453	0.602
0.05	0.388	0.324	0.288	0.224	0.270	0.450	0.350	0.299	0.218	0.215
0.10	0.494	0.465	0.397	0.300	0.344	0.246	0.228	0.189	0.136	0.159
0.20	0.384	0.364	0.336	0.202	0.258	0.083	0.078	0.072	0.042	0.054

RESULTS AND DISCUSSION

Magnesium molybdosilicate shows the cation exchange behaviour. The equilibrium uptake, q_A, of all the metal ions increases with increase in the pH of the external solution, attains a maximum [for Cu^{2+} = 9.5, Zn^{2+} = 10, Cd^{2+} = 10.5, Ni^{2+} = 10.5 and Co^{2+} = 10.5] and then decreases (Tables 1 and 2).

With increase in concentration, q_A and K_d values increase, attain a maximum at 0.10 M concentration and then decrease (Table-3).

The investigated metal ions show the following sequences of q_A:

Cu(II) > Zn(II) > Cd(II) > Co(II) > Ni(II).

The increase in q_A with pH is presumably because increase in concentration of OH$^-$ ions facilitates the release of H$^+$ ions. Decrease in q_A values after an optimum pH at which maximum uptake takes place, is probably because of the competition of excessive NH_4^+ ions with the metal complex ions, as complete ammine complex formation[8] of Cu(II), Zn(II), Cd(II), Ni(II) and Co(II) takes place around pH 9.5, 10.0, 11.0, 11.0 and 10.5, respectively.

The observed increase in q_A with increase in concentration of the exchanging solution is because of increase in the ionic activity[9]. However, the decrease

beyond a certain limit is due to the possible lowering of the ionic activity at very high concentrations. A diminution of exchange potential with decreasing ionic activity is well known[9].

The observed difference in q_A values for the different metal ammine complexes seems to be connected with the combined effect of charge and size, *i.e.*, ionic potential (ϕ) of the exchanging ion. The higher the value of (ϕ), more is the q_A. The investigated metal ions have identical formal charge, *i.e.*, +2, but in the absence of definite knowledge of the structural data of this complex species in aqueous solution, it is reasonable to make some quantitative estimation of the size of the complex ion on the basis of its known symmetry[10] and ionic radius[11] of the central metal atom [Zn(II), 74 pm; Cd(II), 95 pm; Co(II), 65 pm; Ni(II), 69 pm and Cu(II), 73 pm]. Because of known differences in the symmetry of ammine complexes, the dimensions of the simple ions will not solely determine the size of the complex species. Obviously, the tetrahedral symmetry involves a more compact structure than octahedral, *i.e.*, the overall size of $[Zn(NH_3)_4]^{2+}$ and $[Co(NH_3)_4]^{2+}$ complexes will be smaller than $[Ni(NH_3)_6]^{2+}$ and $[Co(NH_3)_6]^{2+}$ complexes. Further, it appears that $[Cu(NH_3)_4]^{2+}$ has got square-planar geometry, thereby probably a laminar structure. So its size if not less, may not be larger than tetrahedral $[Zn(NH_3)_4]^{2+}$ and $[Cd(NH_3)_4]^{2+}$. Thus, the ionic radius of ammine complexes is expected to be:

Cu (square-planar) < Zn (tetrahedral) < Co (octahedral) < Ni (octahedral)

The ionic potential of these will be in the reverse order, *i.e.*,

Cu > Zn > Cd > Co > Ni

This is in agreement with the observed order of q_A.

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