

Sorption studies of some metal ions on zirconium(IV) iodomolybdate

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Distribution coefficients of a large number of metal ions on zirconium(IV) iodomolybdate have been determined as a function of concentration of formic acid. On the basis of K_d values, Hg^{2+} has been separated from numerous metal ions.

Analytical applications of inorganic ion-exchangers have been reviewed by Inczedy¹ and Walton². Separation of mercury from numerous metal ions on an inorganic ion-exchanger has been reported by Gill and Tandon³. Herein distribution coefficients (K_d) of various metal ions on zirconium(IV) iodomolybdate cation-exchanger have been determined as a function of the concentration of formic acid. On the basis of K_d values, Hg^{2+} has been separated from a large number of metal ions on a small column of zirconium(IV) iodomolybdate.

Experimental

Zirconium(IV) bis (nitrate) oxide (BDH), sodium iodate (E Merk) and ammonium molybdate (Koch-Light) were used for the synthesis of ion-exchange material. All other reagents and chemicals were of AR grade.

Preparation of ion-exchanger

Zirconium(IV) iodomolybdate ion-exchanger was synthesized as follows: Aqueous solutions (0.1 M each) of sodium iodate and ammonium molybdate were added to an aqueous solution (0.1 M) of zirconium(IV) bis (nitrate) oxide at pH 1. The desired pH was adjusted by adding dil HNO_3 or NaOH solution⁴. The gel so formed was allowed to settle down for 24 hr, washed several times with demineralized water, filtered under suction and dried at 40°C in an oven. The dried material was treated with demineralized water, so as to obtain the exchanger into smaller particles. This treatment was exothermic in nature. The exchanger was converted into H^+ -form by keeping it in 1.0M HNO_3 for 24 hr, filtered thoroughly and dried at room temperature.

Distribution coefficients

The distribution coefficients (K_d) were determined at various concentrations of formic acid as follows. The exchanger in H^+ -form (0.25g; 50-100 mesh) was treated with $2 \times 10^{-4} M$ metal salt solution in the solute formic acid (25 ml) of varying concentrations (0.10 to 0.60 M). The mixture was allowed to stand until the concentration of cation in the supernatant solution became constant (about 24 hr). The amount of metal species left in the solution was then determined by titrating against standard solution of EDTA. The K_d value, expressed in mlg^{-1} , was calculated in the usual manner⁵.

Separation of metal ions

Quantitative separation of metal ions were achieved on a glass column (int. diam. 0.6 cm) packed with exchanger (2g, 50-100 mesh) in H^+ -form. A metal ion mixture was transferred into the exchanger column. The flow rate of effluent was maintained at 1 ml min^{-1} throughout the elution process.

The metal ion concentration of $2 \times 10^{-4} M$ was used, for the comparison of K_d values; this concentration was very low as compared to the ion-exchange capacity of the material.

Results and discussion

Distribution coefficients were determined at $25 \pm 2^\circ C$ and the values are listed in Table 1. The results suggest that the ion-exchange material is loaded partly with the metal ions, partly with cation complex ions formed with formic acid and partly with hydrogen ions. Here we assume that no neutral or anionic complexes are sorbed on the exchanger. The different K_d values of different metal ions (high, low and constant) in different solute concentrations have been interpreted as follows:

(i) High K_d values for Hg^{2+} : Hg^{2+} forms a coordinately saturated metal complex ion in the solute concentrations range of 0.10-0.20 M and therefore it is highly absorbed on the exchanger.

(ii) Constant and low K_d values of certain metal ions: K_d values of Ba^{2+} , Ca^{2+} , Mg^{2+} , Sr^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} , Al^{3+} , Co^{2+} , VO^{2+} and Mn^{2+} are almost constant and very low in the solute concentration range of 0.10-0.60 M. The low K_d values may be due to the fact that the solute concentration range is not favourable for these metal ions to form coordinately saturated metal complex ions.

Table 1—Distribution Coefficients of Metal Ions on Zirconium(IV) Iodomolybdate (50-100 mesh) at $25 \pm 2^\circ\text{C}$ in Solute of Varying Concentration (0.10-0.60 M formic acid)

| Sl. No | Metal ions | K_d (ml/g) at solute concentration (M) | | | | Useful conc range (M) of formic acid as eluent |
|--------|-------------------------------|--|--------|-------|-------|--|
| | | 0.10 | 0.20 | 0.40 | 0.60 | |
| 1 | Ca ²⁺ | 17.6 | 12.4 | 8.7 | 6.4 | — |
| 2 | Mg ²⁺ | 15.1 | 3.8 | 3.8 | 0.8 | 0.05-0.10 |
| 3 | Sr ²⁺ | 45.1 | 45.1 | 25.4 | 18.1 | — |
| 4 | Ba ²⁺ | 90.6 | 80.0 | 59.4 | 54.3 | 0.05-0.10 |
| 5 | Cu ²⁺ | 18.3 | 5.6 | 5.6 | 5.6 | 0.05-0.10 |
| 6 | Hg ²⁺ | 1820.0 | 1376.9 | 772.7 | 638.5 | — |
| 7 | Zn ²⁺ | 17.5 | 8.0 | 5.6 | 5.6 | 0.05-0.10 |
| 8 | Cd ²⁺ | 46.4 | 18.5 | 13.1 | 11.1 | 0.05-0.10 |
| 9 | Ni ²⁺ | 22.1 | 14.7 | 6.9 | 0.2 | 0.05-0.10 |
| 10 | UO ₂ ²⁺ | 185.2 | 33.3 | 2.6 | 1.0 | — |
| 11 | Al ³⁺ | 44.8 | 24.8 | 16.0 | 14.0 | — |
| 12 | Co ²⁺ | 41.7 | 27.5 | 21.4 | 12.1 | — |
| 13 | VO ²⁺ | 57.5 | 16.3 | 12.8 | 2.2 | 0.05-0.10 |
| 14 | Th ⁴⁺ | 518.2 | 423.1 | 112.5 | 100.0 | 0.40-0.50 |
| 15 | Mn ²⁺ | 30.0 | 26.9 | 24.1 | 9.2 | 0.40-0.50 |
| 16 | La ³⁺ | 137.2 | 126.7 | 92.4 | 61.9 | — |
| 17 | Fe ³⁺ | 175.0 | 151.4 | 100.0 | 31.4 | 0.40-0.50 |

Table 2—Separation of Metal Ions Achieved on Zirconium (IV) Iodomolybdate Columns

| Sl No | Separations achieved | Amount loaded (mg) | Metal (%) eluted | Vol of effluent (ml) | Eluent (HCOOH) used (M) |
|-------|----------------------|--------------------|------------------|----------------------|-------------------------|
| 1 | Cu ²⁺ | 0.3685 | 98.9 | 80 | 0.10 |
| | Hg ²⁺ | 1.1572 | 98.1 | 60 | 1.00 |
| 2 | Ni ²⁺ | 0.2795 | 98.7 | 50 | 0.10 |
| | Hg ²⁺ | 1.1572 | 97.8 | 60 | 1.00 |
| 3 | Zn ²⁺ | 0.3072 | 98.7 | 60 | 0.10 |
| | Hg ²⁺ | 1.1572 | 98.1 | 60 | 1.00 |
| 4 | Th ⁴⁺ | 0.2889 | 98.2 | 40 | 0.50 |
| | Hg ²⁺ | 1.1572 | 97.8 | 60 | 1.00 |
| 5 | Cd ²⁺ | 0.5575 | 97.9 | 60 | 0.10 |
| | Hg ²⁺ | 1.1572 | 97.8 | 60 | 1.00 |
| 6 | VO ²⁺ | 0.2530 | 96.4 | 60 | 0.10 |
| | Hg ²⁺ | 1.1572 | 97.4 | 60 | 1.00 |
| 7 | Ba ²⁺ | 0.6675 | 98.8 | 60 | 0.10 |
| | Hg ²⁺ | 1.1572 | 98.1 | 60 | 1.00 |
| 8 | Mg ²⁺ | 0.1274* | 98.1 | 60 | 0.10 |
| | Hg ²⁺ | 1.1572 | 97.8 | 60 | 1.00 |
| 9 | Mn ²⁺ | 0.2999 | 98.5 | 50 | 0.50 |
| | Hg ²⁺ | 1.1572 | 97.4 | 60 | 1.00 |
| 10 | Fe ³⁺ | 0.2457 | 98.5 | 50 | 0.50 |
| | Hg ²⁺ | 1.1572 | 98.1 | 60 | 1.00 |

(iii) Low K_d values with decreasing trend: K_d values of UO₂²⁺, La³⁺, Fe³⁺ and Th⁴⁺ decrease in this order with increase in the concentration of the solute. At ≤ 0.1 M solute concentration, these metal ions are insufficient to form coordinately saturated metal complexes which can be sorbed by the exchanger. UO₂²⁺, Fe³⁺, La³⁺ and Th⁴⁺ may form coordinately saturated neutral complexes at higher concentrations of the solute that would not be sorbed on the exchanger.

Hg²⁺ is strongly adsorbed on the exchanger, hence a quantitative separation of Hg²⁺ from a number of metal ions has been successfully achieved on a small

column of zirconium(IV) iodomolybdate. The results are shown in Table 2.

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