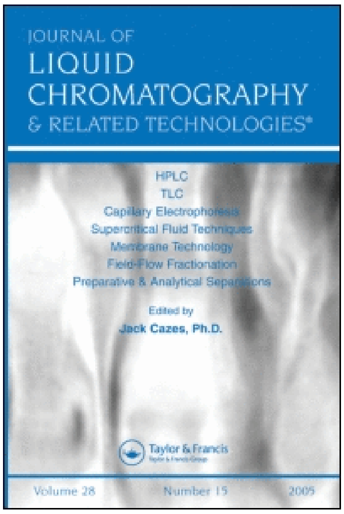

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Studies of Hydrous Zirconium Oxide. I. Thin-Layer Chromatography of Some Metal Ions on Hydrous Zirconium Oxide: Quantitative Separation of Bi(III) from Several other Metal Ions

Asit K. Senl[a]; Sudhangsu B. Das[a]; Uday C. Ghosh[b]
[a] Department of Chemistry, Visva-Bharati, West Bengal, India [b] Department of Chemistry, Durgapur Government College, West Bengal, India

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STUDIES OF HYDROUS ZIRCONIUM OXIDE. I. THIN-LAYER CHROMATOGRAPHY OF SOME METAL IONS ON HYDROUS ZIRCONIUM OXIDE: QUANTITATIVE SEPARATION OF Bi(III) FROM SEVERAL OTHER METAL IONS

Asit K. Sen[1], Sudhangsu B. Das[1], and
Uday C. Ghosh[2]
[1]*Department of Chemistry*
Visva-Bharati, Santiniketan 731 235
West Bengal, India
[2]*Department of Chemistry*
Durgapur Government College
Durgapur, West Bengal, India

ABSTRACT

The analytical potentiality of hydrous zirconium oxide as an ionexchanger has been investigated by thin-layer chromatographic (TLC) technique. Binder-free thin-layers of hydrous zirconium oxide are useful for 25 ternary and 12 quaternary separations. Quantitative separation of Bi (III) from some ternary and quaternary mixtures of metal ions has been achieved.

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INTRODUCTION

In continuation of our work on TLC studies on hydrous stannic oxide (1), in this communication we report the systematic investigation on thin layer chromatography of metal ions using binder free layers of hydrous zirconium oxide. Simple aqueous hydrochloric acid and mixed aqueous organic solvent systems containing hydrochloric acid/nitric acid plus acetone/dioxane/dimethyl sulphoxide have been used. Some important and useful separations containing ternary and quaternary mixture of metal ions have been achieved. A quantitative separation scheme for separation of microgram amount of Bi (III) from the mixture of several metal ions has been developed.

EXPERIMENTAL

Apparatus

Thin layers of hydrous zirconium oxide were prepared on glass plates (20x3cm) which subsequently developed in several solvent systems in glass jars (25x7 cm).

Reagents

Chemicals and solvents used in this work were of analytical grade (B.D.H./E. Merck/S. Merck).

Preparation of Ion-exchange materials on thin layer plates

Hydrous zirconium oxide was prepared by adding 1.0M NH_3 solution to 6.1M $ZrOCl_2$ solution in 0.1M HCl (2:1) with constant stirring (2). The precipitated zirconium oxide was kept with the mother liquor at room temperature for five days for ageing. Then it was filtered, washed with deionised water several times until free from chloride, air dried, and ignited at 300°C into a muffle furnace for an hour. The material was then powdered and slurried with a little deionised water in a mortar. It was then spread over the glass plate with the help of an applicator (1). Almost uniformly thin layers (0.1 mm thickness) were obtained, which were ready for use after drying in air. These plates gave reproducible R_F values.

Test solutions

The test solutions in general had a metal concentration of 4mg/ml (nitrate/chloride).

Detection reagents

(a) Yellow ammonium sulphide solution : Pb(II), Ag(I), Hg(II), Tl(I), Bi(III).

(b) 0.05% benzidine in 10% acetic acid : Mn(II), Au(III).

(c) dithizone (1-2 mg) in 100 ml CCl_4 : Cd(II), Zn(II).

(d) 1% ethanolic dimethylglyoxiome : Ni(II).

(e) 5% KI solution : Pt(IV).

(f) 6.2% rubeanic acid : Co(II), Cu(II).

Solvent systems

The following solvent systems were used in these studies.

1. 0.1M HCl adjusted to pH 1, 2 and 3.
2. Dioxane : 0.1M HCl = (1:1), (1:2), (2:5) (v/v)
3. Acetone : 0.1M HCl = (1:1), (1:2), (2:5) (v/v)
4. Acetone : 0.1M HNO_3 = (1:1), (1:2), (2:5) (v/v).

It was found that, in presence of mixed DMSO-HCl, the thin layers tended to split off the plates. Hence this solvent was avoided in our work.

PROCEDURE

One or two drops of the test solutions were placed on the plates with thin glass capillaries. The spots were allowed to dry and developed in different solvent systems. Solvent front was allowed to rise 11cm in each case. R_T and R_L values were measured as usual after detection.

For quantitative work, a stock solution of bismuth nitrate /‾Bi(III) - 5000 µg/ml_7 was prepared and standardized complexometrically with the disodium salt of EDTA (3) solution. The known amount of synthetic mixture containing Bi(III) was applied with the help of a micropipette on the line of application. The plates were developed in acetone-HNO_3 system. A pilot plate was run simultaneously to locate the position of Bi(III) by detecting with yellow ammonium sulphide. The area corresponding to Bi(III) was scratched out (4) from the working plate and Bi(III) was determined spectrophotometrically by iodide method (5).

RESULTS AND DISCUSSION

The results of our TLC studies reveal that most of the metal ions have appreciable R_F values both in dilute HCl and in mixed solvent system containing dioxane/acetone plus HCl/HNO_3. The general trend in R_F values is that some of the metal ions have lower R_F values in HCl system than HNO_3 system. This is consistent with the expectation. Hydrous zirconium oxide acts as a cation exchanger as well as an anion exchanger. It acts as an anion exchanger in acid medium. The probable equilibria are

$$\overline{ZrO_2.x\,H_2O} \overset{H^+}{\rightleftharpoons} \overline{ZrO_2.(x-1)H_2O.H^+} + H_2O$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$\overline{ZrO_2\ (x-1)H_2O.H^+} + OH^- + H^+ \rightleftharpoons \overline{ZrO_2(x-1)H_2O.H^+ \ldots OH^-} + H^+$$

The bars refer in exchanger.

The anionic chlorocomplexes of some metals are strongly adsorbed by the exchanger in HCl medium and hence R_F values of these metal ions are small.

The R_F values of metal ions which do not form chlorocomplexes decrease with increase of pH of the solvent system. When hydrous zirconium oxide acts as a cation exchanger, its cation exchange property increase with increase of pH of the solvent system and thus the decrease of R_F values is evident.

$$\overline{ZrO_2 . xH_2O} \xrightleftharpoons{OH^-} \overline{ZrO_2\ (x-1)H_2O.OH^-} + H_2O$$

$$\overline{ZrO_2\ (x-1)\ H_2O.OH^-} + H^+ + OH^- \rightleftharpoons \overline{ZrO_2\ (x-1)\ H_2O.OH^-\ ...}\ \ H^+ + OH^-$$

The bars refer in exchanger.

In mixed solvent systems all the metal ions except Bi(III), Ag(I) and Pt(IV) are moved up from the base line (Table 1 and 2). On the basis of this quantitative separation of Bi(III) from several other metal ions in the mixture has been made (Table 3). All the results given in Table 1,2 and 3 are the average of triplicate runs. Moreover, the separations in acetone-HNO_3 system (after development) are much better defined and sharper than those obtained

TABLE 1

Ternary Separations Achieved on Hydrous Zirconium Oxide Thin-Layer.

Solvent system-Acetone : 0.1M HNO_3 = 1:2 (v/v)
Time - 2 hours

Separations achieved (R_T-R_L)
Bi(III)(0-0)-Au(III) (0.20-0.23) - Mn(II)(0.88-0.95)
Bi(III)(0-0)-Au(III) (0.20-0.22) - Co(II)(0.8-0.88)
Bi(III)(0-0)-Au(III) (0.20-0.22) - Ni(II)(0.85-0.92)
Bi(III)(0-0)-Au(III) (0.1-0.15) - Zn(II)(0.65-0.85)
Bi(III)(0-0)-Au(III) (0.1-0.16) - Cd(II)(0.6-0.72)
Bi(III)(0-0)-Au(III) (0.1-0.16) - Tl(I)(0.6-0.7)
Bi(III)(0-0)-Cu(II) (0.3-0.5) - Mn(II)(0.85-0.9)
Bi(III)(0-0)-Cu(II) (0.3-0.5) - Co(II)(0.8-0.9)
Bi(III)(0-0)-Cu(II) (0.2-0.7) - Zn(II)(0.8-0.9)
Bi(III)(0-0)-Cu(II) (0.2-0.6) - Cd(II)(0.65-0.7)
Bi(III)(0-0)-Cu(II) (0.2-0.6) - Tl(I)(0.6-0.7)
Ag(I)(0-0) -Au(III) (0.1-0.15) - Mn(II)(0.82-0.9)
Ag(I)(0-0) -Au(III) (0.22-0.23) - Co(II)(0.79-0.88)
Ag(I)(0-0) -Au(III) (0.20-0.23) - Ni(II)(0.86-0.95)
Ag(I)(0-0) -Au(III) (0.1-0.15) - Zn(II)(0.8-0.85)
Ag(I)(0-0) -Au(III) (0.1-0.15) - Tl(I) (0.55-0.7)
Ag(I)(0-0) -Cu(II) (0.2-0.65) - Mn(II)(0.85-0.94)
Ag(I)(0-0) -Cu(II) (0.3-0.5) - Co(II)(0.78-0.92)
Ag(I)(0-0) -Cu(II) (0.2-0.7) - Ni(II)(0.85-0.93)
Ag(I)(0-0) -Cu(II)(0.2-0.7) - Zn(II)(0.74-0.85)
Pt(IV)(0-0) -Au(III) (0.12-0.14) - Mn(II)(0.83-0.9)
Pt(IV)(0-0) -Au(III)(0.1-0.12) - Co(II)(0.7-0.9)
Pt(IV)(0-0) -Au(III)(0.13-0.18) - Ni(II)(0.75-0.95)
Pt(IV)(0-0) -Au(III)(0.1-0.16) - Zn(II)(0.65-0.8)
Pt(IV)(0-0) -Au(III)(0.12-0.15) - Cd(II)(0.6-0.7)

TABLE 2

Quaternary Separations Achieved on Hydrous Zirconium Oxide Thin-Layer

Solvent system - Acetone : 0.1M HNO_3 = 1:2 (v/v)
Time - 2 hours

Separations achieved (R_T-R_L)
Ag(I)(0-0)-Hg(II)(0.15-0.17)-Pb(II)(0.25-0.29)-Mn(II)(0.85-0.92)
Ag(I)(0-0)-Hg(II)(0.15-0.2)-Pb(II)(0.25-0.28)-Co(II)(0.86-0.93)
Ag(I)(0-0)-Hg(II)(0.15-0.18)-Pb(II)(0.25-0.3)-Ni(II)(0.85-0.95)
Ag(I)(0-0)-Hg(II)(0.15-0.2)-Pb(II)(0.28-0.32)-Zn(II(0.7-0.8)
Ag(I)(0-0)-Hg(II)(0.15-0.18)-Pb(II)(0.2-0.25)-Cd(II)(0.75-0.78)
Ag(I)(0-0)-Hg(II)(0.15-0.17)-Pb(II)(0.25-0.28)-Tl(I)(0.6-0.7)
Bi(III)(0-0)-Hg(II)(0.18-0.2)-Pb(II)(0.25-0.3)-Mn(II)(0.86-0.95)
Bi(III)(0-0)-Hg(II)(0.18-0.2)-Pb(II)(0.28-0.32)-Co(II)(0.85-0.94)
Bi(III)(0-0)-Hg(II)(0.15-0.18)-Pb(II)(0.25-0.3)-Ni(II)(0.82-0.92)
Bi(III)(0-0)-Hg(II)(0.15-0.18)-Pb(II)(0.28-0.32)-Zn(II)(0.7-0.82)
Bi(III)(0-0)-Hg(II)(0.15-0.18)-Pb(II)(0.25-0.28)-Cd(II)(0.75-0.85)
Bi(III)(0-0)-Hg(II)(0.16-0.18)-Pb(II)(0.25-0.3)-Tl(I)(0.65-0.75)

TABLE 3

Quantitative Separation of Bi(III) from Ternary and Quaternary Mixtures of Metal Ions.

Bi(III) added = 20.00 µg in each experiment

Solvent system - Acetone : 0.1M HNO_3 = 1:2 (v/v)
Time - 2 hours

Sl. No.	Mixture taken	Amount of the other metal ion applied (µg)	Amount of Bi(III) recovered (µg)	Percentage of error
1.	Bi(III)	-	20.16	+ 0.80
2.	Bi(III)-Au(III)-Ni(II)	Au(III)(5.0)-Ni(II)(5.4)	19.5	- 2.5
3.	Bi(III)-Au(III)-Zn(II)	Au(III)(5.0)-Zn(II)(5.0)	20.0	0
4.	Bi(III)-Au(III)-Tl(I)	Au(III)(5.0)-Tl(I) (5.2)	19.83	- 0.85
5.	Bi(III)-Au(III)-Co(II)	Au(III)(5.0)-Co(II)(5.0)	20.0	0
6.	Bi(III)-Au(III)-Cd(II)	Au(III)(5.0)-Cd(II)(5.9)	20.16	+ 0.8
7.	Bi(III)-Au(III)-Mn(II)	Au(III)(5.0)-Mn(II)(5.0)	19.83	- 0.85
8.	Bi(III)-Hg(II)-Pb(II)-Co(II)	Hg(II)(5.0)-Pb(II)(5.0)-Co(II)(5.8)	20.33	+ 3.35
9.	Bi(III)-Hg(II)-Pb(II)-Mn(II)	Hg(II)(5.0)-Pb(II)(5.0)-Mn(II)(5.5)	19.83	- 0.85
10.	Bi(III)-Hg(II)-Pb(II)-Ni(II)	Hg(II)(5.0)-Pb(II)(5.0)-Ni(II)(5.1)	18.83	- 5.85
11.	Bi(III)-Hg(II)-Pb(II)-Zn(II)	Hg(II)(5.0)-Pb(II)(5.0)-Zn(II)(5.4)	20.16	+ 0.8
12.	Bi(III)-Hg(II)-Pb(II)-Tl(I)	Hg(II)(5.0)-Pb(II)(5.0)-Tl(I)(5.1)	19.33	- 3.35
13.	Bi(III)-Hg(II)-Pb(II)-Cd(II)	Hg(II)(5.0)-Pb(II)(5.0)-Cd(II)(5.2)	19.83	- 0.85

in acetone-HCl system. Quantitative separations of Ag(I) from ternary and quaternary mixtures and Pt (IV) from binary and ternary mixtures can also be done. The noteworthy separations are Bi(III)-Cu(II)-Zn(II), Bi(III)-Cu(II)-Mn(II), Ag(I)-Au(III)-Ni(II), Ag(I)-Cu(II)-Zn(II), Ag(I)-Cu(II)-Ni(II), Pt(IV)-Au(III)-Ni(II), Pt(IV)-Au(III)-Cu(II), Ag(I)-Hg(II)-Pb(II)-Zn(II), Bi(III)-Hg(II)-Pb(II)-Tl(I), Ag(I)-Hg(II)-Pb(II)-Tl(I).

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