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Thin-Layer Chromatography of 49 Metal Ions on Stannic Antimonate in Aqueous and Mixed Solvent Systems Containing Dimethylsulfoxide: Quantitative Separation of Uranium from Numerous Metal Ions

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Abstract

Thin-layer chromatography of 40 metal ions in 31 aqueous and mixed solvent systems has been performed on stannic antimonate ion-exchange material. Dimethylsulfoxide has been utilized to resolve such binary mixtures as La^{3+} and Ce^{3+} from Pr^{3+}, Nd^{3+}, and Sm^{3+}; VO^{2+} from Ti^{4+}, Nb^{5+}, and Ta^{5+}; Ga^{3+} from In^{3+}, Tl^{+}, and Y^{3+}; Fe^{3+} from VO^{2+}; and Mg^{2+} from Al^{3+}.

Quantitative separation of 200 to 800 μg U from its binary mixtures and from the synthetic mixtures containing Mg^{2+}, Bi^{3+}, Fe^{3+}, Th^{4+}, Ce^{4+}, Cr^{3+}, Zr^{4+}, Hf^{4+}, Ti^{4+}, Mn^{2+}, Cu^{2+}, Ce^{3+}, In^{3+}, Y^{3+}, Ca^{2+}, Co^{2+}, Tl^{+}, Nb^{5+}, and Ag^{+} has been obtained.

INTRODUCTION

Thin-layer chromatography, while widely used in organic analysis, has received only restricted application in inorganic chemistry. Seiler and

co-workers (*1–6*) were the first to explore its potential in the separation of inorganic substances. Brinkman (*7*) has recently reviewed the studies performed in this direction which indicate that most research is concentrated on silica gel and a few have been reported (*8–22*) on the use of inorganic ion exchange materials. These suffer from two limitations: (a) in almost all cases a binder such as silica gel, starch, or cellulose has been used which clouds the interpretation of the mechanism; and (b) quantitative aspects of inorganic analysis have not been properly investigated (*23*).

Stannic antimonate is known to possess some unusual and promising ion-exchange properties (*24*), and we have demonstrated its utility in paper chromatography using solvent systems containing dimethylsulfoxide (DMSO) (*25*) and also in electrophoretic studies of inorganic ions (*26*). This article summarizes our efforts to use thin layers of this material which have been prepared without any binder. As a result, certain very important and difficult separations which could not be effected by the two above-mentioned techniques on this material are now possible using DMSO–HNO_3 and DMSO–HCl solvent systems. A quantitative separation of uranium from numerous metal ions has also been achieved. DMSO has been used because of its excellent solvating and complex-forming ability which has been successfully utilized earlier in paper chromatography (*25*).

EXPERIMENTAL

Apparatus

Stannic antimonate thin layers were prepared on glass plates (15 × 3 cm), and the plates were developed in glass jars (20 × 5 cm). Spectrophotometric studies were performed on a Bausch and Lomb Spectronic-20 colorimeter.

Reagents

Chemicals and solvents used were of analytical grade from B.D.H., England.

Preparation of the Ion Exchange Material and Thin-Layer Plates

Stannic antimonate in the H^+ form, prepared according to the procedure described earlier (*24*), was powdered and slurried with a little demineralized water in a mortar. It was then spread over the glass plates with

the help of an applicator, and uniform thin layers (~0.1 mm thick) were obtained. The thickness of the layers was checked with a spherometer. The plates were ready for use after drying in air.

Test Solutions and Detection Reagents

The test solutions were generally 0.1 *M* in metal chloride or nitrate. Conventional spot test reagents were used for detection purposes (*25*).

Procedure

For qualitative studies, one or two drops of the test solutions were placed on plates with thin glass capillaries. After drying the spots, development was made in different solvent systems and the ascent was fixed as 11 cm in all cases. R_T and R_L values were measured as usual after detection.

For quantitative work, a stock solution of uranium (100,000 ppm) was prepared in distilled water by dissolving uranyl nitrate, and the standard spectrophotometric method using H_2O_2 as the coloring reagent (*27*) was set up. Known amounts of uranium along with the other metal ions were spotted with the help of a lambda pipette, and the development was performed in the chosen solvent systems. A pilot plate was run simultaneously in order to locate the exact position of the spot on the working plate. The area where uranium was located was scratched, and uranium was eluted with 4 *M* HNO_3. The exchanger was separated from the solution by filtration and was washed four or five times with 4 *M* HNO_3 to ensure complete elution of uranium. The filtrate was evaporated to dryness and the residue dissolved in a little distilled water. The uranium was then determined spectrophotometrically (*27*).

RESULTS

The following solvent systems were used in these studies.

1. Pure DMSO
2. DMSO + 6 *M* HNO_3 (1 : 1)
3. DMSO + 3 *M* HNO_3 (1 : 1)
4. DMSO + 1 *M* HNO_3 (1 : 1)
5. DMSO + 0.5 *M* HNO_3 (1 : 1)
6. DMSO + 0.1 *M* HNO_3 (1 : 1)
7. DMSO + 0.01 *M* HNO_3 (1 : 1)

8. DMSO + 1.4 *M* HCl (1 : 1)
9. DMSO + 1.2 *M* HCl (1 : 1)
10. DMSO + 1 *M* HCl (1 : 1)
11. DMSO + 0.8 *M* HCl (1 : 1)
12. DMSO + 0.6 *M* HCl (1 : 1)
13. DMSO + 0.4 *M* HCl (1 : 1)
14. DMSO + 0.2 *M* HCl (1 : 1)
15. DMSO + water (1 : 1)
16. HNO_3 (10^{-5} *M*, 10^{-3} *M*, 10^{-2} *M*, 10^{-1} *M*, 0.5 *M*, 1 *M*, 2 *M*, 8 *M*, 10 *M*, 12 *M*, 14 *M*, and 15 *M*)
17. 0.1 *M* $HClO_4$
18. Water

Table 1 summarizes the separations achieved on stannic antimonate thin layers, while Tables 2 and 3 show the quantitative results.

TABLE 1

Separations Actually Achieved on Stannic Antimonate Thin Layers in Different Solvent Systems

Solvent system	Metal ion separation ($R_T - R_L$)	Time (hr)
DMSO + 6 *M* HNO_3 (1 : 1)	La^{3+} (0.0–0.20) – Pr^{3+} (0.74–1.00)	6
	La^{3+} (0.00–0.18) – Nd^{3+} (0.70–1.00)	
	La^{3+} (0.00–0.20) – Sm^{3+} (0.76–1.00)	
	Ce^{3+} (0.00–0.00) – Pr^{3+} (0.72–1.00)	
	Ce^{3+} (0.00–0.00) – Nd^{3+} (0.80–1.00)	
	Ce^{3+} (0.00–0.00) – Sm^{3+} (0.78–1.00)	
	Th^{4+} (0.00–0.20) – UO_2^{2+} (0.85–1.00)	
	Ti^{4+} (0.00–0.00) – VO^{2+} (0.75–1.00)	
	Nb^{5+} (0.00–0.00) – VO^{2+} (0.75–1.00)	
	Ta^{5+} (0.00–0.00) – VO^{2+} (0.75–1.00)	
	In^{3+} (0.00–0.00) – Ga^{3+} (0.80–1.00)	
	Tl^{+} (0.00–0.18) – Ga^{3+} (0.80–1.00)	
	Y^{3+} (0.00–0.00) – Ga^{3+} (0.80–1.00)	
DMSO + 3 *M* HNO_3 (1 : 1)	Fe^{3+} (0.00–0.00) – VO^{2+} (0.80–1.00)	6
	Fe^{3+} (0.00–0.00) – Be^{2+} (0.85–1.00)	
	Mg^{2+} (0.00–0.20) – Al^{3+} (0.75–1.00)	
12 *M* HNO_3	Cd^{2+} (0.00–0.00) – Hg^{2+} (0.85–0.95)	2
	Zn^{2+} (0.00–0.00) – Hg^{2+} (0.85–1.00)	
	Tl^{+} (0.22–0.32) – Al^{3+} (0.00–0.00)	

TABLE 2

Quantitative Separation of Uranium in Binary Mixtures

Sample no.	Mixture	Amount of U applied (μg)	Amount of U formed (μg)	Percentage error
1	U–Mg^{2+}	400	400	0.0
2	U–Bi^{3+}	400	370	−7.5
3	U–Th^{4+}	400	390	−2.5
4	U–Ce^{3+}	400	450	12.5
5	U–Ti^{4+}	400	370	−7.5
6	U–In^{3+}	400	370	−7.5
7	U–Y^{3+}	400	450	12.5
8	U–Cr^{3+}	400	400	0.0
9	U–Mn^{2+}	400	400	0.0
10	U–Hf^{4+}	400	400	0.0

TABLE 3

Quantitative Separation of Uranium from Synthetic Mixtures

Sample no.	Amount of U applied (μg)	Amount of U found (μg)	Percentage error	Standard deviation (parts per thousand)
1	400	400	0.0	
2	400	390	−2.5	11.8
3	400	390	−2.5	
4	600	600	0.0	
5	600	600	0.0	
6	600	580	−3.3	11.0
7	600	610	1.6	
8	600	600	0.0	

The following two synthetic mixtures were prepared by taking 1 ml each of the cation solutions along with uranium; (a) Mg^{2+}, Bi^{3+}, Fe^{3+}, Th^{4+}, Ce^{4+}, Cr^{3+}, Zr^{4+}, Hf^{4+}, Ti^{4+}, and Mn^{2+}; and (b) Cu^{2+}, Ce^{3+}, In^{3+}, Y^{3+}, Ca^{2+}, Co^{2+}, Tl^{+}, Nb^{5+}, and Ag^{+}.

DISCUSSION

These studies reveal that only a few metal ions move on stannic antimonate thin layers with some appreciable R_F values. In pure DMSO only

uranium moves to the solvent front. With the addition of HNO_3 the movement of cations generally increases, and in solvent No. 2 (DMSO + 6 *M* HNO_3, 1 : 1) some cations such as Be, Al, Ga, U, V, K, Rb, Cs, Pr, Nd, and Sm move to an appreciable extent. In solvent systems Nos. 9 to 14, in which HCl has been mixed with DMSO, the movement of cations is more suppressed than in solvent system Nos. 1 to 8.

In the aqueous solvent systems containing low concentration of HNO_3 (0.5 *M*), the metal ions generally do not move. This may be due to the high selectivity of stannic antimonate for metal ions. As the HNO_3 concentration is increased, the metal ions start moving, obviously due to the increased H^+ ion concentration. The best results are obtained in 12 *M* HNO_3. Addition of DMSO to the nitric acid systems enhances the R_F values. In this respect, thin layers of stannic antimonate behave in the same manner as its papers (*25*). This is probably due to the decrease in the ionization constant of stannic antimonate by the presence of DMSO. The behavior of uranium (UO_2^{2+}) is quite interesting. It moves to a great extent in most of the solvent systems except for a few in which the acid concentration is very small. In aqueous HNO_3 systems it moves only when the HNO_3 concentration is more than 0.25 *M*. Uranyl nitrate is highly soluble in organic solvents and forms a soluble complex $UO_2(NO_3)_2 \cdot 2DMSO$ (*28*) with DMSO. DMSO–HCl solvent systems are not helpful in the movement of the metal ions. On comparison with the results of our paper chromatographic studies (*25*), we observe generally lower R_F values in TLC. Greater total ion-exchange capacity of the glass plates than of the papers may be responsible for this difference.

Table 2 summarizes some important binary separations which have been actually achieved. To mention a few, we have successfully separated La^{3+} and Ce^{3+} from Pr^{3+}, Nd^{3+}, and Sm^{3+}; VO^{2+} from Ti^{4+}, Nb^{5+}, and Ta^{5+}; and Ga^{3+} from In^{3+}, Tl^+, and Y^{3+} in DMSO + 6 *M* HNO_3 (1 : 1). Similarly, Fe^{3+}–VO^{2+} and Mg^{2+}–Al^{3+} can be separated in DMSO + 3 *M* HNO_3 (1 : 1). The unique behavior of UO_2^{2+} in these studies enabled us to separate it from numerous metal ions quantitatively (Tables 2 and 3). In order to check the reproducibility of our results, four different quantities of uranium (200, 400, 600, and 800 μg) were mixed in different synthetic mixtures and the uranium estimated. The best results were obtained when the mixture contained 400 or 600 μg U.

The refluxing effect of stannic antimonate was also checked, and it was found that the results are not much different if we use a sample refluxed in the mother liquor for 40 hr.

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