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CHELATION ION CHROMATOGRAPHY ON DMSO IMPREGNATED SILICA GEL-G LAYERS: SPECIFIC SEPARATION OF Cd^{2+} , W^{6+} , AND Zr^{4+} FROM TRANSITIONAL METAL IONS

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ABSTRACT

Chelation ion chromatography of metal ions on DMSO impregnated silica gel-G layers in ether; DMSO: 1M HNO_3 (1:1); n-butanol: acetone: HNO_3 (6:6:1) and di-isopropyl ether: DMSO: THF systems having varying compositions, was performed. The zero R_f for a number of cations is explained in terms of precipitation and strong adsorption. It was possible to separate Cd^{2+} , W^{6+} , Zr^{4+} , Zn^{2+} and VO^{2+} from numerous metal ions. A number of analytically important binary and ternary separations were also achieved and were found useful in synthetic alloy analysis.

INTRODUCTION

Zirconium alloys are widely used in many fields of modern technology and therefore the separation of zirconium from other

metals is important. The separation of cadmium from zinc is of great interest because of close resemblance in their chromatographic behaviour. Cadmium was included in the 'black list' proposed by 'European Economic Community' in 1975 for substances requiring priority attention because of their toxicity, persistence and bioaccumulation in the aquatic environment. The toxic potential of cadmium has recently been emphasized in the water quality criteria proposed by the U.S. Environment Protection Agency. Tungston increases the density of alloys to which it is added. It is used to obtain steels with great wear resistance and special resistance to tempering.

The use of ligands for the separation of metal ions on silica gel-G thin layers has received some attention in recent years¹⁻⁹. Dimethyl sulfoxide (DMSO) has a complex forming ability with almost all metal ions and was first used to impregnate silica gel-G layers for the separation of sugar acetates¹⁰. However, the complexing ability of DMSO has not been utilized for the separation of metal ions on impregnated silica gel-G layers. The present study is an effort in this direction.

EXPERIMENTAL

Apparatus:

Thin layer chromatography applicator of Toshniwal (India) was used to prepare thin layers on 20x3.5cm glass plates. Glass jars (20x6cm) were used for development.

Reagents:

Silica gel-G, DMSO, Ether, Di-isopropyl ether, THF, n-Butanol and Acetone were all of analytical grade from B.D.H. or E. Merck.

Test Solutions and Detectors:

Test solutions, 0.1 M chlorides, nitrates or sulphates of cations were prepared in a little amount of the corresponding acids. Conventional spot-test reagents were used for detection purposes¹¹.

Preparation of DMSO impregnated silica gel-G thin layers:

The slurry was prepared by mixing silica gel-G with conductivity water in the ratio of 1:3 with constant stirring for about 5 min. This slurry was immediately coated on the clean glass plates with the help of an applicator and uniform thin layers (~0.15 mm thick) were obtained. The plates were first dried at room temperature and then in an electric oven for 2 hrs at $100 \pm 5^\circ\text{C}$. These plates were stored in an oven at room temperature. Silica gel-G layers were then impregnated with 1:1 mixture of DMSO and sulphur free toluene. The plates were then heated in an oven until the dampness has just disappeared leaving the silica layer with an even opaque white appearance. The plates are then kept in an air tight glass cabinet to cool, where they could be stored before use. The samples of separation were applied as rapidly as possible so as to exclude moisture and to protect the layers from damage.

Procedure:

The sample solution was loaded (1 or 2 spots) on DMSO impregnated silica gel-G layers with the help of glass capillaries and the spots were allowed to dry at room temperature. The solvent ascent was 11cm. The R_f values were measured after detection.

Solvent Systems:

The following solvents were used:

S₁ Ether

S ₂	DMSO : 1M HNO ₃ (1:1)
S ₃	n Butanol: Acetone: HNO ₃ (6:6:1)
S ₄	Di-isopropyl ether:DMSO (10:1)
S ₅	DMSO: THF (1:10)
S ₆	Di-isopropyl ether: DMSO: THF (9:1:1)
S ₇	Di-isopropyl ether: DMSO: THF (7:1:3)
S ₈	Di-isopropyl ether: DMSO: THF (5:1:5)
S ₉	Di-isopropyl ether: DMSO: THF (3:1:7)
S ₁₀	Di-isopropyl ether: DMSO: THF (1:1:9).

RESULTS AND DISCUSSION

Thin layer chromatography of metal ions on DMSO impregnated silica gel-G layers leads to useful separations. The R_f values of all the metal ions on unimpregnated and impregnated layers are summarised in Table I. Important binary separations are possible on these layers. A cursory inspection of the R_f data on impregnated layers (Table I) reveals two interesting points:

1. For most of the cations studied, the R_f value suddenly increases when the THF concentration is more than 90% in the given solvent system. This may be due to the fact that THF being polar, solvates the cation or cation-DMSO complexes causing higher R_f , e.g. the R_f value of Zr^{4+} is zero till the solvent composition is 3:1:7 (S₉). The R_f value now increases gradually with the rise in percentage of THF in the solvent media and becomes 0.1 in the solvent (S₅) having composition 0:1:10. This may be due to the high percentage of THF which solvates the Zr -DMSO complex. ZrO^{2+} forms $ZrO \cdot 8DMSO^{2+}$ complex¹⁴.

TABLE I
R_f values of metal ions in different solvent systems.

Metal ions	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	S ₇	S ₈	S ₉	S ₁₀											
	U.M. M.	U.M. M.	U.M. M.	U.M. M.	U.M. M.	U.M. M.	U.M. M.	U.M. M.	U.M. M.	U.M. M.											
Tl ⁺	0.00	0.00	N.D.	0.15	0.55	0.60	0.00	0.00	0.75	-	0.00	0.00	0.10	0.14	0.11	0.60	0.00	0.20	0.14	0.10	
V ²⁺	0.45	0.00	0.93	0.98	0.75	0.75	0.10	0.05	0.15	0.15	0.00	0.11	0.00	0.00	0.08	0.15	0.15	0.06	0.15	0.13	0.18
Cr ³⁺	T	0.00	0.85	0.96	0.55	0.50	0.15	0.00	0.15	0.10	0.10	0.10	0.00	0.15	T	0.15	0.90	0.02	0.15	0.10	0.17
Mn ²⁺	0.25	0.00	0.95	0.94	0.65	0.70	0.00	0.00	0.40	0.12	0.00	0.20	0.02	0.00	0.00	0.00	0.10	0.00	0.08	0.20	0.18
Fe ³⁺	0.05	0.00	0.85	0.90	0.65	0.65	0.00	0.08	0.15	0.00	0.02	T	0.04	T	0.05	0.00	0.00	0.00	0.25	0.06	0.00
Co ²⁺	0.05	0.00	0.95	0.98	0.55	0.60	0.00	0.00	0.25	0.00	0.07	0.00	0.11	0.00	0.10	0.24	0.02	0.18	0.10	0.15	0.15
Ni ²⁺	0.00	0.45	0.95	0.98	0.75	0.90	0.75	0.00	0.15	T	0.12	0.00	0.12	0.00	0.25	0.10	0.02	0.00	0.15	0.00	0.00
Cu ²⁺	0.00	0.00	0.95	0.97	0.60	0.75	0.00	0.00	0.30	0.00	0.16	0.10	0.15	0.00	0.15	0.10	0.02	0.00	0.10	0.10	0.10
Zn ²⁺	0.22	0.00	0.95	0.92	0.65	0.75	0.11	0.00	0.21	T	0.00	0.14	0.16	0.10	0.00	1.00	0.04	0.88	0.05	0.30	0.30
Zr ⁴⁺	0.00	0.12	0.95	0.05	0.25	0.50	0.00	0.07	0.10	0.48	0.00	0.18	0.00	0.00	0.00	0.00	0.00	0.00	0.14	0.07	0.40
Nb ⁵⁺	0.00	0.00	0.86	T	0.95	0.90	0.00	T	0.30	0.30	0.00	0.20	0.15	0.10	0.25	0.10	0.35	0.58	0.10	0.45	0.45
Mo ⁶⁺	0.00	0.00	0.95	0.98	0.55	0.55	0.00	0.34	0.00	0.00	0.00	0.36	0.00	0.00	0.00	0.40	0.00	T	0.00	0.12	0.12
Ru ³⁺	N.D.	0.00	N.D.	0.95	N.D.	N.D.	0.00	0.00	0.00	0.00	0.00	0.05	0.10	0.10	0.02	0.08	0.01	0.04	0.00	0.90	0.90
Rh ³⁺	0.00	0.05	0.95	N.D.	0.95	0.80	0.00	0.00	0.55	0.70	0.15	0.00	0.00	0.08	0.37	0.08	0.40	0.00	0.14	0.30	0.30
Pd ²⁺	0.00	0.00	0.95	0.94	0.85	0.85	0.00	0.05	0.40	0.95	0.00	0.10	0.00	0.00	0.16	0.20	0.15	0.00	0.25	0.20	0.20
Ag ⁺	0.00	0.18	0.95	0.10	T	0.40	0.15	0.00	0.50	0.95	0.15	0.00	0.00	0.00	0.15	0.20	0.11	0.75	0.25	0.20	0.20
Cd ²⁺	0.17	0.00	0.65	0.98	0.80	0.75	0.00	0.00	0.45	T	0.00	0.00	0.00	0.00	0.00	0.80	0.10	0.00	T	0.08	0.08
La ³⁺	0.00	0.00	0.92	T	0.75	0.75	0.05	N.D.	0.00	0.90	0.00	0.40	0.00	0.20	0.00	0.10	0.00	0.35	0.00	0.30	0.30
Ta ⁵⁺	0.00	0.00	0.95	0.14	0.65	0.70	0.00	N.D.	0.16	0.8	0.00	0.00	0.00	N.D.	0.00	N.D.	0.00	N.D.	0.07	N.D.	N.D.
W ⁶⁺	0.00	0.00	T	N.D.	0.00	0.10	0.00	0.00	0.00	T	0.00	T	0.00	0.00	T	0.00	0.08	0.00	0.00	0.00	0.00
Pt ⁴⁺	0.00	0.00	0.90	0.99	0.80	0.90	0.08	0.96	0.27	T	0.00	0.00	0.00	0.00	0.22	0.40	0.26	0.30	0.38	0.34	0.34
Au ³⁺	0.08	0.78	0.95	0.89	0.85	0.95	0.26	0.48	0.35	0.40	0.08	T	0.45	0.35	0.86	0.45	0.25	0.65	0.35	0.80	0.80
Hg ₂ ²⁺	0.15	0.00	0.95	0.95	0.95	0.90	0.85	0.00	0.35	0.50	0.45	0.10	0.75	0.85	0.75	0.80	0.10	0.00	0.15	0.15	0.15
Hg ²⁺	0.16	0.76	0.90	0.92	0.80	0.75	0.65	0.70	0.95	0.75	0.26	0.78	0.57	0.89	0.56	0.30	0.76	T	0.95	0.95	00.85

M- Impregnated
U.M.- Unimpregnated
T- Tailing
N.D.- Not detected.

2. The R_f value of Cu^{2+} is higher than that of Fe^{3+} , which is almost zero. This may be attributed to the large size of Fe^{3+} complex compared to that of copper. Copper forms $\text{Cu}(\text{DMSO})_4^{2+}$ while iron forms $\text{Fe}(\text{DMSO})_6^{3+}$ complex¹².

In general, the ions which have zero R_f value may do so owing to (a) precipitation (b) strong adsorption due to high charge. On mixing solutions of the cations with DMSO followed by the addition of solvent ether, it was found that for Ag^+ , Ni^{2+} , Co^{2+} , Cu^{2+} , W^{6+} , Mo^{6+} , Ti^{4+} , La^{3+} and Zr^{4+} , a precipitate was obtained. In such cases, zero R_f may be due to precipitation mechanism. In order to simulate conditions on silica gel-G thin layers, DMSO was added to the cation solution followed by the solvent. A number of ions precipitate under these conditions (Table II). In these cases precipitation mechanism holds good.

In order to study the effect of DMSO impregnation on R_f values of metal ions, a comparison has been made of the migration of cations on impregnated and unimpregnated layers in di-isopropyl ether: DMSO: THF systems of varying compositions. The studies led to the following conclusions:

- (i) The R_f values for most of the cations are higher on unimpregnated layers than on impregnated ones except for Ni^{2+} , Cu^{2+} and Rh^{3+} .
- (ii) In DMSO: THF (1:10), the R_f values of Ti^{4+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Cu^{2+} , Cd^{2+} and Hg^{2+} on impregnated layers are higher than on unimpregnated ones. This may be due to the higher

T A B L E - II
PRECIPITATION OF CATIONS IN THE SOLVENTS USED

SOLVENT	CATIONS WHICH PRECIPITATE	CATIONS WHICH DO NOT PRECIPITATE
S ₁	Ag ⁺ , Ni ²⁺ , Co ²⁺ , Cu ²⁺ , W ⁶⁺ , Mo ⁶⁺ , Ti ⁴⁺ La ³⁺ , Zr ⁴⁺	Pd ²⁺ , Pt ⁴⁺ , Rh ³⁺ , Nb ⁵⁺ , Ta ⁵⁺
S ₃	NIL	W ⁶⁺
S ₄	W ⁶⁺ , Mo ⁶⁺ , Cd ²⁺	Fe ³⁺ , Pd ²⁺ , Co ²⁺ , Mn ²⁺ , Cu ²⁺ , Ti ⁴⁺ , Rh ³⁺ , La ³⁺ , Nb ⁵⁺ , Ta ⁵⁺ , Zr ⁴⁺ , Ru ³⁺
S ₆	W ⁶⁺ , Mo ⁶⁺ , Cd ²⁺	Pd ²⁺ , Mn ²⁺ , Pt ⁴⁺ , Zn ²⁺ , Ti ⁴⁺ , La ³⁺ , Nb ⁵⁺ , Ta ⁵⁺ , Zr ⁴⁺ , Ru ³⁺
S ₇	W ⁶⁺ , Cd ²⁺ , Mo ⁶⁺	Ag ⁺ , VO ²⁺ , Pd ²⁺ , Pt ⁴⁺ , Rh ³⁺ , La ³⁺ , Ta ⁵⁺ , Zr ⁴⁺ , Ru ³⁺
S ₈	W ⁶⁺ , Cd ²⁺ , Mo ⁶⁺	Mn ²⁺ , Zn ²⁺ , La ³⁺ , Ta ⁵⁺ , Zr ⁴⁺ , Ru ³⁺
S ₉	W ⁶⁺ , Mo ⁶⁺	Fe ³⁺ , Ni ²⁺ , Co ²⁺ , Mn ²⁺ , Cr ³⁺ , Ti ⁴⁺ , La ³⁺ , Ta ⁵⁺ , Zr ⁴⁺ , Ru ³⁺
S ₁₀	W ⁶⁺ , Mo ⁶⁺	La ³⁺ , Ru ³⁺
S ₅	W ⁶⁺ , Mo ⁶⁺	La ³⁺ , Ru ³⁺

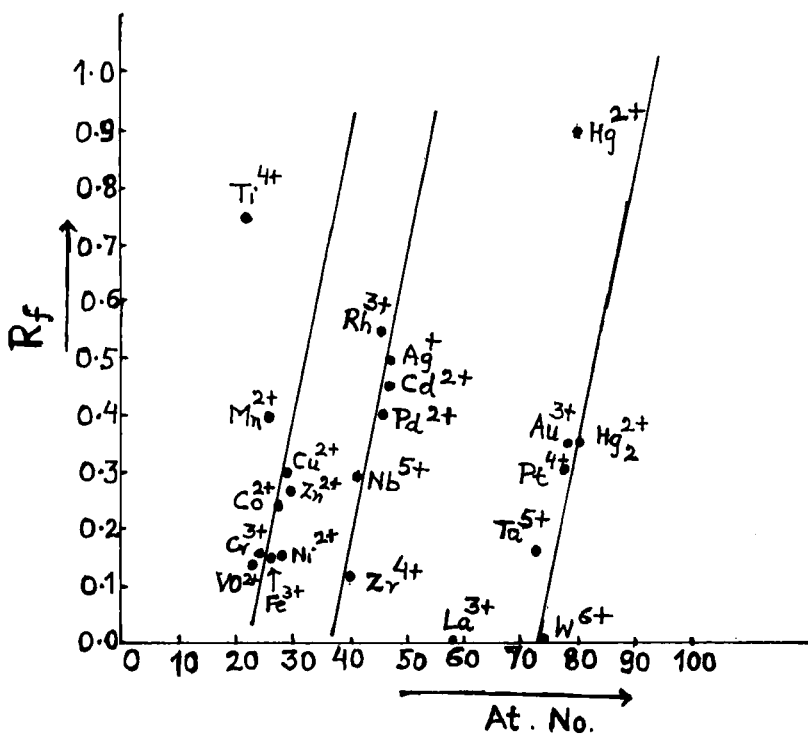


FIG. 1 Plot of R_f versus Atomic Number in Di-isopropylether:DMSO:THF (0:1:10).

T A B L E - III

SEPARATION OF ONE CATION FROM NUMEROUS METAL IONS ON DMSO IMPREGNATED SILICA GEL-G LAYERS.

SOLVENT	METAL ION SEPARATED FROM	IONS THAT INTERFERE
S_1	VO^{2+}	Zn^{2+} , Cr^{3+} , Mn^{2+} .
S_1	Zn^{2+}	VO^{2+} , Cr^{3+} , Mn^{2+} , Cd^{2+}
S_2	Cd^{2+}	W^{6+}
S_3	W^{6+}	Ag^+
S_3	Zr^{4+}	Ag^+

proportion of THF in the solvent media which solvates the DMSO complexes of these ions causing higher R_f .

A plot of R_f versus atomic number (Fig.1) in DMSO:THF (1:10) on impregnated layers shows that almost all transition metals fall on a straight line. This indicates that in case of these metals the R_f is proportional to the atomic number which may be attributed to their similar chemical nature.

The most outstanding achievement of the above study is the separation of one cation from numerous metal ions (Table III). Zirconium is separated from vanadium and twenty one other transition metal ions in n-butanol:acetone:HNO₃ (6:6:1) system. The only interfering ion is Ag⁺. The separation of Cd²⁺ from Zn²⁺ and from twenty one other metal ions in DMSO: 1 M HNO₃ (1:1) has been achieved. Similarly W⁶⁺ is separated from twenty two other metal ions in n-butanol: acetone: HNO₃ (6:6:1) system and Zn²⁺ is separated from nineteen other metal ions in ether media. Out of these, the separation of Cu²⁺ from Zn²⁺, Cu²⁺ from Zn²⁺ and Fe³⁺, Cu²⁺ from Zn²⁺ and Mg²⁺, Cu²⁺ from Ni²⁺ and W⁶⁺, Bi³⁺ from Pb²⁺, Sn⁴⁺ and Cd²⁺ is important in alloy analysis.

In order to establish the utility of these separations, the synthetic alloy samples of Cu²⁺ with Zn²⁺, Fe³⁺, Mg²⁺, Ni²⁺ and W⁶⁺ (Muntz metal, Delta or Aichmetal, Elektron metal, German Silver and Platinoid) and alloy sample of Bi³⁺ with Pb²⁺, Sn⁴⁺ and Cd²⁺ (Wood's Alloy) were prepared by mixing various metallic solutions in certain ratios so that they correspond to the actual metallic proportions in the standard alloys, and then these samples were tried on silica gel-G layers and the metal ion separations were achieved.

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