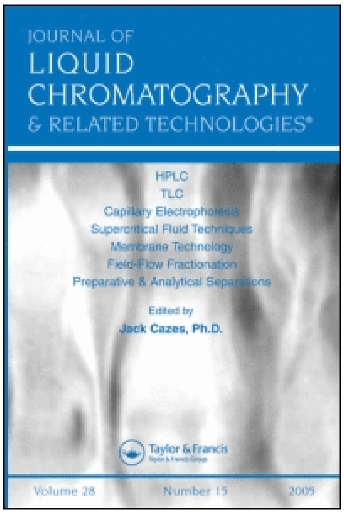

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THIN-LAYER CHROMATOGRAPHIC SEPARATION OF DMSO COMPLEXES OF METAL IONS

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SUMMARY

Thin layer chromatography of DMSO complexes of some metal ions in a large number of solvent systems was carried out. The specific separation of DMSO complex of Hg^{2+} from others have been achieved in ethyl acetate media. Other important separations of metal - DMSO complexes are :- Ni^{2+} - Co^{2+}, Ce^{3+} - La^{3+} and Zn^{2+} - Mn^{2+}. Some other possible separations are also reported.

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INTRODUCTION

The dipolar aprotic solvent dimethyl sulphoxide (DMSO) is a liquid over a wide range of temperatures, is a strong electron donor, and has a high polarity. It is therefore an excellent and selective solvent for many organic and even polymeric compounds, and can enter into H - bonding and dipole - dipole association. The structure of DMSO with a "hard" oxygen atom and a "soft' sulfur atom has a complex forming tendency with almost all metal ions leading to good solvation of cations and poor solvation of anions. Owing to its unusual properties as solvent, it offers numerous advantages as an eluant in cation exchange chromatography. Since 1968, a large number of papers on ion exchange chromatography have appeared pointing to the excellent solvating properties of DMSO (1-10). Our earlier studies (11-13) also support this view. Interestingly, DMSO has also been used as a stationary phase in thin layer partition chromatography (14).

Recently, we have reported the paper chromatographic separations of DMSO complexes of metal ions (15). Since silica gel is more convenient than cellulose for spreading as thin layers and is also resistant to heat and to vigrous detecting reagents, it was thought that silica gel might be the most useful support for the chromatography of metal-DMSO complexes. The present work was therefore under taken and the results are summarized in the following pages.

EXPERIMENTAL

Apparatus - A thin layer chromatography apparatus (Toshniwal, India) for the preparation of Silica Gel-G thin layers on 20 x 3.5 cm. glass plates was used. The chromatography was performed in 24x6 cm glass jars.

Reagents - Chemicals and solvents used were of AnalaR grade.

Test Solutions and Detectors - Test solutions, the DMSO complexes of Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, UO_2^{2+}, Hg^{2+}, Mn^{2+}, Al^{3+}, Cr^{3+}, Cu^{2+} and Th^{4+} were prepared as reported by Cotton and Francis (16). The complexes of Fe^{3+} and of La^{3+} and Ce^{3+} were prepared by the methods reported earlier (17,18). These were dissolved in DMSO.

The complexes of Hg^{2+} and Cd^{2+} were detected with yellow ammonium sulphide solution. Fe^{3+}, Cu^{2+} and UO_2^{2+} zones were detected with aqueous $K_4Fe(CN)_6$ solution. 1% alcoholic diphenyl carbazide was used to detect the complexes of Zn^{2+}, Mn^{2+} and Cr^{3+}. Al^{3+} complexes was detected with auqeous Aluminon solution. 1% ammonical dimethyl glyoxime was used to detect Ni^{2+} and Co^{2+} zones. The complexes of La^{3+}, Ce^{3+} and Th^{4+} were detected with 1% alcoholic alizarine Red-S.

Preparation of silica gel-G layers - The slurry used was prepared by mixing silica gel-G in D.M.W. in the ratio of 1:3 with constant shaking for about 5 min. This slurry was immediately coated on clean glass plates with the help of an applicator and uniform thin layers (0.15mm thick) were obtained. The plates were first allowed to dry at room temperature and then in an electric oven at $100 \pm 5^{\circ}C$ for 2 hrs. These were then stored in an oven at room temperature.

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

RESULTS

Numerous solvent systems, where there was no fear of breaking the complex were tried to achieve the separation of metal - DMSO complexes. Useful results are summarized in Table 1. The R_f values of only those metal - DMSO complexes which give compact spots are reported. The TLC of metal - DMSO complexes reveals the possibility of a number of interesting separations. eg. separations of Hg^{2+}, Al^{3+}

Fe^{3+}, Cu^{2+} and UO_2^{2+} from other metal - complexes are possible in all solvent systems except benzene and nitrobenzene. Zn^{2+} and Th^{4+} can be separated from Hg^{2+}, Ni^{2+}, Co^{2+}, Ce^{3+} & La^{3+} in most of the solvents tried. Separation of Zn^{2+} and Mn^{2+} complexes from each other is clearly visible in De-mineralized water and that of Ni^{2+} from Co^{2+} complexes in Di methyl formamide. Specific separation of Hg^{2+} from all other metal - DMSO complexes have actually been achieved in ethyl acetate media. Some other separations are also evident from Table 1.

DISCUSSION

The thin layer chromatography of the metal complexes of DMSO, a unique solvent possessing excellent complex forming ability, proved difficult and posed few problems owing to the following reasons:

(i) Only those solvants are chosen which has less complex forming ability than DMSO as the metal - DMSO complexes are not very stable. The order of co-ordinating ability (19) towards typical cations for some of the solvents tried is given as -

$$\text{DMSO} > \text{DMF} > H_2O > (CH_3)_2CO > C_6H_5NO_2$$

(ii) Non-polar solvents can not be used or can be used in mixtures with water as the metal - DMSO complexes are soluble only in water like systems. This is evidenced by the Zero - R_f values for all metal - DMSO complexes in benzene (Table - 1).

TABLE 1

R_f values of metal - DMSO complexes on Silica gel - G layers

Cation Complexes	Water	Methyl Alcohol	DMF	Ethyl Alcohol	Water: Alcohol: Acetone 2:1:1	Acetone	n-propyl Alcohol	n-Butyl Alcohol	Ethyl Acetate	Benzene	Nitro-Benzene
Al^{3+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe^{3+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cu^{2+}	0.07	0.15	0.15	0.15	0.12	0.00	0.07	0.10	0.07	0.00	0.00
UO_2^{2+}	0.00	0.05	0.05	0.10	0.07	0.10	0.05	0.08	0.10	0.00	0.00
Cd^{2+}	0.37	0.48	0.45	0.45	T	T	0.42	0.45	0.00	0.00	0.00
Hg^{2+}	0.57	0.95	0.95	0.92	0.95	0.94	0.90	0.92	0.85	0.70	0.00
Ni^{2+}	0.82	0.20	0.20	0.45	T	0.20	T	T	0.00	0.00	0.00
Co^{2+}	0.65	T	0.70	0.58	T	T	T	0.33	0.10	0.00	0.00
Zn^{2+}	0.15	0.19	0.20	T	T	T	0.20	0.17	0.00	0.00	0.00
Mn^{2+}	0.50	0.25	0.27	0.30	0.27	0.20	0.15	0.22	0.00	0.00	0.00
Cr^{3+}	0.25	0.50	0.40	0.45	0.37	0.35	0.20	0.30	0.00	0.00	0.00
Th^{4+}	0.15	0.22	0.20	0.25	0.20	0.07	0.00	0.00	0.00	0.00	0.00
Ce^{3+}	0.40	0.30	T	0.35	0.42	0.47	0.62	0.65	0.00	0.00	0.00
La^{3+}	0.50	0.47	0.45	T	0.50	0.00	0.65	0.60	0.00	0.00	0.00

T = Tailing

The TLC of metal - DMSO complexes is very interesting. The complexes of La^{3+} and Ce^{3+} are soluble in methyl alcohol, acetone and Dimethyl formamide but the same are insoluble in benzene and nitro-benzene(20, 21) showing thereby a significant R_f values in these solvents and a zero R_f value in benzene and nitrobenzene. The zero R_f values for all other metal - DMSO complexes in benzene and nitrobenzene may be attributed to this solubility phenomenon. In all the solvent systems studied, the R_f value of Cu^{2+} complex is always higher than the Fe^{3+} complex. This is probably due to the relatively smaller size of the Cu^{2+} complex with DMSO. Copper forms $Cu\ (DMSO)_4^{2+}$ while iron forms $Fe(DMSO)_6^{3+}$ complexes (22).

On the basis of R_f values, some selective separations can be developed. The separation of DMSO complexes of Hg^{2+} from others is an important one and have been achieved experimentally in ethyl acetate media. Ni^{2+} and Co^{2+} complexes were separated from each other in DMF. The separation of complexes of Ce^{3+} from La^{3+} was actually achieved in acetone.

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