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## PAPER CHROMATOGRAPHIC SEPARATION OF DMSO COMPLEXES OF METAL IONS

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### A B S T R A C T

$R_f$  values of DMSO complexes of some metal ions in twelve solvent systems are given. The separation of Zn and Hg DMSO complexes from others have been achieved in Water and in n-butyl alcohol respectively by using paper chromatography. Some other possible separations are also reported.

### I N T R O D U C T I O N

Dimethyl sulphoxide (DMSO) offers numerous advantages as an eluant in cation exchange chromatography; it has a complex forming tendency with almost all metal ions, contains no ionizable protons and has a fairly high dielectric constant ( $\epsilon = 47.5$ ). It has attracted the attention of researchers because of it's biological applications and its unusual properties as solvent, i.e.; its ability to solvate metal ions in preference to anions and a specific solvating effect.

DMSO was first introduced as an eluant in ion exchange chromatography by Janauer (1) who used it for the determination of  $K_d$  on Dowex 50 W - x 8 resin using 0.10 - 1.20 M HCl in 20 - 95% DMSO. Janauer (2), Brize (3), Fritz (4) and Phipps (5) studied the ion exchange behaviour of a large number of cations in mixed solvent systems containing DMSO. Blasius and Schmitt (6) studied the sorption behaviour of various cation exchangers in DMSO -  $H_2O$  mixtures. Later Smits and Co-workers (7,8) made a detailed study of Ca and Mg on Dowex 50 W - x 8 in DMSO -  $H_2O$  - HCl systems. Qureshi et. al. (9) determined the  $K_d$  values of a number of cations in DMSO and DMSO - Formic acid systems and separated, U, Y, La and Ce from Th. They studied (10) the chromatographic behaviour of 48 metal ions in DMSO -  $H_2O$  -  $HNO_3$  systems. Our earlier studies (11-13) have also pointed out to the excellent solvating properties of DMSO.

Paper chromatographic separations of EDTA complexes of metal ions have been reported earlier (14). However, no effort has been made to separate the DMSO complexes of metal ions. The present work was therefore undertaken and the results are summarized in the following pages.

### EXPERIMENTAL

Apparatus - Chromatography was performed on Whatman No - 1 Papers of 15 x 3.5 cm in 22 x 5 Cm jars using the ascending technique.

Reagents - Chemicals and solvents used were of Analar grade.

Preparation of Metal - DMSO Complexes - 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 (15). The Complexes of  $\text{Fe}^{3+}$  and of  $\text{La}^{3+}$  and  $\text{Ce}^{3+}$  were prepared by the methods reported earlier (16, 17). These were dissolved in DMSO.

Detectors - The complexes of  $\text{Hg}^{2+}$  and  $\text{Cd}^{2+}$  were detected with yellow ammonium sulphide solution.  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{UO}_2^{2+}$  zones were detected with aqueous  $\text{K}_4\text{Fe}(\text{CN})_6$  solution. 1% alcoholic diphenyl carbazide was used to detect the complexes of  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Cr}^{3+}$ .  $\text{Al}^{3+}$  - complex was detected with aqueous Aluminon solution. 1% ammonical dimethyl glyoxime was used to detect  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  zones. The complexes of  $\text{La}^{3+}$ ,  $\text{Ce}^{3+}$  and  $\text{Th}^{4+}$  were detected with 0.1% alcoholic alizarine Red - S.

Procedure -

One spot of nearly 0.1 M solutions of DMSO complexes of metal ions was applied on the paper with a thin glass capillary. The paper was then conditioned for 20 min. and the developer was allowed to ascend 11 cm. in all cases.

R E S U L T S

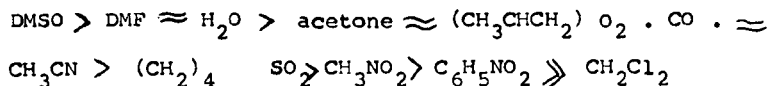
Twelve solvent systems were tried to achieve the separation of metal - DMSO complexes. The results are summarized in table 1. The  $R_f$  values of only those metal - DMSO complexes which give compact spots are reported. A cursory inspection of the movements of metal - DMSO complexes reveals that a number of interesting separations are possible, e.g.,  $\text{Cd}^{2+}$  and  $\text{UO}_2^{2+}$  can be separated from  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$  and  $\text{Al}^{3+}$  in Ethyl alcohol.  $\text{Cd}^{2+}$  from  $\text{Al}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Th}^{4+}$ ,  $\text{UO}_2^{2+}$  and  $\text{Cu}^{2+}$  in n-propyl alcohol and  $\text{Hg}^{2+}$  from other metal complexes in n - Butyl alcohol, acetone and ethyl acetate systems.  $\text{Zn}^{2+}$  can be

separated from  $\text{Cr}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{La}^{3+}$  using water as developer. Separations of  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Th}^{4+}$  and that of  $\text{Cd}^{2+}$ ,  $\text{La}^{3+}$ ,  $\text{Co}^{2+}$  and  $\text{Ce}^{3+}$  from other metal complexes are possible in water : Acetone (1:1) and in water; Acetone: Alcohol (2:1:1) systems respectively. Only those solvent systems where there was no fear of breaking the complex were tried.

### D I S C U S S I O N

The separation of DMSO complexes of metal ions is important since DMSO is extensively used as a solvent and possesses excellent complex forming ability. The paper chromatography of metal - DMSO complexes pose some problems owing to the following reasons.

- (a) Metal - DMSO complexes are not very stable, hence only those solvents are chosen which has less complex forming ability than DMSO. The Solvation of simple cations is essentially the process of forming complexes in which the ligands are solvent molecules. The order of co-ordinating ability (18) towards typical cations for some common solvents is given as -



- (b) Metal - DMSO complexes are soluble only in water like systems, hence non-polar solvent can not be used or can be used in mixtures with water. This is evidenced by the Zero  $R_f$  values for all metal - DMSO complexes in benzene (Table - 1).

TABLE 1

R<sub>f</sub> values of Metal - DMSO Complexes

Solvent Systems	Complexes of						Th <sup>4+</sup>
	Cr <sup>3+</sup>	Cd <sup>2+</sup>	Cu <sup>2+</sup>	UO <sub>2</sub> <sup>2+</sup>	Hg <sup>2+</sup>	Ce <sup>3+</sup>	
1. Methyl alcohol	0.00	0.65	0.00	0.00	0.52	0.73	0.00
2. Ethyl alcohol	T	0.47	0.04	0.53	0.60	0.28	0.19
3. n-Propyl alcohol	0.17	0.49	0.02	0.03	0.54	0.27	0.11
4. n-Butyl alcohol	0.15	0.10	0.00	0.00	0.52	0.08	0.00
5. Water	0.98	0.89	0.53	0.39	0.70	0.93	T
6. Acetone	0.05	0.09	0.00	0.00	0.85	0.25	0.26
7. Ethyl acetate	0.00	0.00	0.00	0.00	0.45	0.00	0.00
8. Dimethyl formamide	0.48	0.62	0.30	0.75	0.70	0.70	0.23
9. Water:Acetone (1:1)	0.56	0.74	0.25	0.16	0.78	0.85	0.10
10. Water:Acetone:Alcohol (2:1:1)	0.79	0.71	0.00	0.00	0.62	0.71	0.00
11. Benzene	0.00	0.00	0.00	0.00	0.02	0.00	0.00
12. Nitro benzene	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Continued.....

The paper chromatography of Metal - DMSO complexes is very interesting. The rare earth metal - DMSO complexes e.g. La and Ce, are soluble in CH<sub>3</sub>OH, acetone and Dimethyl formamide but the same are insoluble in benzene and Nitrobenzene (19,20). This is the reason why the complex of La and Ce show a significant R<sub>f</sub> values in these solvents and a Zero R<sub>f</sub> value in benzene and nitrobenzene. The Zero R<sub>f</sub> value for all

Table 1 continued .....

Solvent Systems	Fe <sup>3+</sup>	Ni <sup>2+</sup>	Complexes of			Co <sup>2+</sup>	La <sup>3+</sup>
			Mn <sup>2+</sup>	Zn <sup>2+</sup>	Al <sup>3+</sup>		
1. Methyl alcohol	0.00	0.73	0.00	T	0.00	0.60	0.68
2. Ethyl alcohol	0.10	0.27	0.22	0.12	0.14	0.52	0.37
3. n-Propyl alcohol	0.00	T	T	T	0.00	0.35	0.10
4. n-Butyl alcohol	0.00	0.05	0.03	0.00	0.00	0.11	0.03
5. Water	0.32	T	0.47	0.05	0.18	0.86	0.79
6. Acetone	0.00	0.04	0.00	0.00	0.00	0.19	0.00
7. Ethyl acetate	0.00	0.00	0.00	0.00	0.00	0.12	0.00
8. Dimethyl formamide	0.15	0.40	0.55	0.35	0.05	0.45	0.64
9. Water:Acetone(1:1)	0.00	T	T	T	0.00	0.80	0.77
10. Water:Acetone:Al- cohol (2:1:1)	0.00	0.64	0.40	T	0.00	0.65	0.67
11. Benzene	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12. Nitro benzene	0.00	0.00	0.00	0.00	0.00	0.00	0.00

T = Tailing

the other metal - DMSO complexes in benzene and nitrobenzene may be attributed to this property.

In case of Cu<sup>2+</sup> and Fe<sup>3+</sup> complexes, the R<sub>f</sub> value of the former in water is higher than that of later. Copper forms Cu (DMSO)<sub>4</sub><sup>2+</sup> while iron forms Fe (DMSO)<sub>6</sub><sup>3+</sup> complexes (21). The lower R<sub>f</sub> value of Fe<sup>3+</sup> complex is due to the larger size of the complex compared to that of copper.

The results show that some important and selective separations can be developed on the basis of the R<sub>f</sub> values.

A number of possible separations have been described in the preceding pages. Out of all these, the separations of DMSO complexes of  $\text{Hg}^{2+}$  and  $\text{Zn}^{2+}$  from others are important ones and have actually been achieved experimentally.

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