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ELECTROCHROMATOGRAPHIC SEPARATION OF DMSO COMPLEXES OF METAL IONS

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ABSTRACT

Electrochromatography of DMSO complexes of fourteen metal ions have been performed in five electrolytes at 100 volts for 3 hrs. The mechanism of migration has been explained and a number of separations of metal-DMSO complexes were achieved.

INTRODUCTION

Dimethyl sulphoxide (DMSO) has attracted the attention of researchers owing to its biological applications and specific solvating effect. 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. It is an excellent and selective solvent for many organic and even polymeric compounds. In the last two decades, it has been extensively used as an eluant in cation exchange chromatography owing to its unusual properties as a solvent. Besides, DMSO has also been used as a stationary phase in thin layer partition chromatography (1).

We have recently reported the paper chromatographic and thin layer chromatographic separations of DMSO complexes of metal ions (2,3). In order to explore further separation

possibilities, the electrochromatography of these metal -DMSO complexes is performed. The results are summarized in following pages.

EXPERIMENTAL

Apparatus :

Electrochromatography was performed on 36.5x2.50cm Whatman No. 1 paper strips with a horizontal strip apparatus.

Reagents and Chemicals :

Chemicals and solvents used were B.D.H. analytical grade reagents.

Preparation of metal-DMSO complexes and detectors :

As described earlier (3).

Procedure :

In all cases electrochromatography was continued for 3 hrs. at a constant potential difference of 100 volts. The current was 4.40 milliamperes. No significant heating was observed during electrophoresis.

RESULTS

In all fourteen metal - DMSO complexes were studied. Only the electrolytes, where there was no fear of breaking the complex were tried. The electrochromatography of metal - DMSO complexes reveals the possibility of a number of interesting separations. The metal - DMSO complexes were separated as a result of opposite migration or differential migration. The movement of the centre of the zone is measured in cm. A positive sign indicates the movement of the metal complex towards the cathode i.e. positively charged species, and a negative sign indicates movement towards the anode i.e. negatively charged species. (Table I). Thus the separations of Co^{2+} , La^{3+} , Mn^{2+} and Ni^{2+} from other metal complexes are possible in demineralized water, methanol and ethanol. The separation of Zn^{2+} from Ni^{2+} and Mn^{2+} complexes and of Cu^{2+} from Cd^{2+} complex is clearly visible in demineralized water. Specific separation of Co^{2+} from all other metal-DMSO complexes have actually been achieved in propanol-2. Zn^{2+} -DMSO complex was also separated from all other complexes in methanol media.

Table - I

Electrophoretic migration of Metal-DMSO Complexes (in cm.)

	Metal Complexes	Background Electrolyte				
		Water	Methanol	Ethanol	Propanol-2	Butanol-1
1.	Cd ²⁺	+ 4.0	- 1.3	0.0	0.0	0.0
2.	Cu ²⁺	+ 1.5	- 1.5	0.0	0.0	0.0
3.	UO ₂ ²⁺	0.0	+ 1.5	0.0	0.0	0.0
4.	Hg ₂ ²⁺	0.0	- 2.2	- 2.0	0.0	0.0
5.	Ce ³⁺	0.0	+ 5.0	0.0	0.0	0.0
6.	Th ⁴⁺	+ 9.0	0.0	0.0	0.0	0.0
7.	Fe ³⁺	0.0	+ 2.0	0.0	0.0	0.0
8.	Ni ²⁺	+ 5.8	+13.0	+ 5.0	0.0	0.0
9.	Mn ²⁺	+ 6.0	+11.5	+12.8	0.0	0.0
10.	Cr ³⁺	- 6.5	+ 2.5	+ 1.5	0.0	0.0
11.	Zn ²⁺	0.0	+ 7.5	+ 4.8	0.0	0.0
12.	Al ³⁺	0.0	0.0	0.0	0.0	0.0
13.	Co ²⁺	+ 8.2	+14.0	+13.5	+ 5.2	0.0
14.	La ³⁺	+10.0	- 3.8	+10.0	0.0	0.0

In ethanol media, specific separation of Ni²⁺, Co²⁺ and Mn²⁺ from other metal complexes have been achieved.

DISCUSSION

In the electrochromatography of metal complexes of DMSO, non polar solvents cannot be used or can be used in mixtures with water as the metal - DMSO complexes are soluble only in water like systems.

The rare earth metal - DMSO complexes e.g. La³⁺ and Ce³⁺, are soluble in water and methanol (4) and hence these metal complexes show a higher migration than other complexes in these solvents. The only exceptions are Ni²⁺, Co²⁺ and Mn²⁺. The lower migration of Fe³⁺ complex than the Cu²⁺ complex in water is probably due to the larger size of

Fe^{3+} complex than the Cu^{2+} - complex. Cu^{2+} forms $\text{Cu}(\text{DMSO})_4^{2+}$ while Fe^{3+} forms $\text{Fe}(\text{DMSO})_6^{3+}$ complexes (5). Similarly the zero migration of Al^{3+} complex in all the media may be due to formation of larger Al^{3+} complex such as $\text{Al}(\text{DMSO})_6^{3+}$ (6). The zero migration for all metal - DMSO Complexes in propanol-2 and butanol-1 may be attributed to the much less solubility of metal - DMSO complexes in these media.

On the basis of electrophoretic migration of these metal - DMSO complexes, some important and selective separations can be developed. A number of possible separations have been described in the preceding pages. The separations of DMSO complexes of Mn^{2+} , Ni^{2+} and Co^{2+} from the other metal complexes are important ones and have actually been achieved experimentally.

The most interesting feature of the above study is the decrease in the migration of the metal-DMSO complexes as one proceeds from methanol to butanol-1. The migration of the metal complexes in different solvents is in the following order.

Methanol > Ethanol > Propanol-2 > Butanol-1

This can be due to the increase in the size of the solvated complex resulting in decreasing migration.

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