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Thin Layer Ionophoresis of D-Block Metal Ions in Aqueous Solutions of Complex Forming Acids and Their Sodium Salts: Specific Separation of Pd²⁺ and Pt⁴⁺ from Numerous Metal Ions

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**THIN LAYER IONOPHORESIS OF d-BLOCK
METAL IONS IN AQUEOUS SOLUTIONS OF
COMPLEX FORMING ACIDS AND THEIR
SODIUM SALTS: SPECIFIC SEPARATION OF
Pd²⁺ AND Pt⁴⁺ FROM NUMEROUS
METAL IONS**

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ABSTRACT

Thin layer ionophoresis of d-block metal ions was studied at 100 volts for 3 h. Aqueous solutions of citric, tartaric and oxalic acids and their sodium salts were chosen as background electrolyte. The mechanism of migration is explained in terms of precipitation and adsorption. There is no significant heating during ionophoresis. Pd²⁺ and Pt⁴⁺ were separated from numerous metal ions.

INTRODUCTION

In 1946, consden, Gorden and Martin¹ carried out the electrophoretic separation of a mixture of amino acids and peptides on silica gel-G thin layers. This technique was not paid proper attention for almost a decade and paper electrophoresis was much in use due to being extremely simple

to carry out. There was a resurgence of interest in the field of thin layer electrophoresis when EGON STAHL had shown how to prepare and use thin layers of adsorbent.

Thin layer electrophoresis has the following two advantages over paper electrophoresis:

- a- Interfering adsorption effect can be avoided by selecting an appropriate adsorbent.
- b- The more uniform and finer structure of the adsorbent used for thin layer electrophoresis some times leads to better resolutions.

Thin layer electrophoresis has since been extensively employed for the separation of organic substances²⁻¹¹. However, little work has been done in the field of separation of inorganic substances. Dobici et al¹² in 1963 was the first to separate iodate and periodate on gypsum thin layers at 400 volts. MOGHISSI¹³ separated inorganic cations and anions using radionuclides on thin layers of kieselguhr by low and high voltage thin layer electrophoresis. Makrova and Stepanov¹⁴ separated Ce, Pm and Eu in a complexon III solution on silica gel and cellulose by thin layer electrophoresis.

The above studies suffer from the following limitations-

- (i) No systematic effort has been made to study the ionophoresis of the d-block metal ions.
- (ii) The complexing acids were not used which enhance the separation potential of the technique.

It was therefore, decided to study the thin layer ionophoresis of d-block metal ions in complexing acids as background electrolytes. The present report summarises such a study.

MATERIALS AND METHODS

Chemicals and Reagents: Chemicals and solvents used were either E.Merck or B.D.H. AnalaR grade. Silica gel-G used to prepare thin layers is of chromatographic grade.

Apparatus : A horizontal electrophoretic set up (Bio-chem India Ltd.) was used for metal ion separations. Glass plates (2.5x25 cm) were used as the support.

Test Solutions and Detectors : Test solutions 0.1 M of chlorides, nitrates or sulphate of cations were prepared in a little amount of the corresponding acids. Conventional spot test reagents were used for detection purposes.¹⁵

Preparation of Silica gel-G Plates : 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 2h. at $100 \pm 5^{\circ}$. These plates were then stored in an oven at room temperature and used as such for ionophoresis.

procedure : The electrophoresis apparatus was filled to the mark with background electrolyte. The electrode compartments are filled to equal heights and apparatus was placed on a horizontal level to remove the siphoning effect. Activated silica gel-G plates, which form the stabilization medium, were placed in position and allowed to become saturated with the electrolyte. Where upon, a small drop (0.02 ml) of the test solution containing 2.10^{-6} moles of the ions was applied separately, with the help of thin glass capillaries, on each glass plate in the middle. In all cases electrochromatography was continued for 3h at a constant potential difference of 100 V. The current was 4.40 milli-ampere. There was no significant heating during electrophoresis.

RESULTS

d-block metal ions were electrochromatographed on silica gel-G layers using following background electrolytes.

SI	0.1 M Oxalic acid.
SII	0.1M Citric acid.
SIII	0.1M Tartaric acid.
SIV	0.1M Oxalic acid + 0.1M Sodium Oxalate (1:1).
SV	0.1M Citric acid + 0.1M Sodium citrate (1:1).
SVI	0.1M Tartaric acid + 0.1M Sodium tartarate (1:1).
SVII	0.1M Nitric acid.

The migration of the centre of the zones were measured in cm. A positive sign indicates the movement of the ion towards the anode and a negative sign towards the cathode. The ionophoretic migration of all the metal ions studied are given in TABLE I. The ionophoresis was also studied in 0.1M nitric acid for comparison with other background electrolytes. Some useful separations were also achieved in nitric acid medium.

DISCUSSION

The ionophoretic studies of metal ions on silica gel-G layers gave interesting results which are summarised in TABLE I. Binary and ternary separations are thus shown to be possible on these layers. In some cases, it is possible to separate one metal ion from a large number of other cations. The salient features of the above study are:

- (1) The majority of cations move towards the cathode showing that most of the metal ions form positively charged complexes with the background electrolytes used.
- (2) Ions which have zero migration may do so owing to (a) precipitation, (b) Complexation to form uncharged complexes, (c) Strong adsorption owing to high charge.

On mixing solutions of the cations with the background electrolyte oxalic acid, it was found that for Au^{3+} and Mo^{6+} a precipitate was obtained. In such cases, zero migration may be due to precipitation mechanism. In order to simulate conditions on thin layers, background

TABLE I

IONOPHORETIC MIGRATION OF METAL IONS IN DIFFERENT ELECTROLYTES ON SILICA GEL-G LAYERS. (In Cm.)

Metal Ions	SI	SII	SIII	SIV	SV	SVI	SVII
Ti ⁴⁺	N.D.	0.0	+4.0	-2.0	-1.0	-7.0	-8.0
VO ²⁺	-2.5	-2.0	+4.0	-2.0	-1.4	-2.5	-4.5
Cr ³⁺	-5.0	0.0	0.0	-1.6	-2.0	-2.0	-4.0
Mn ²⁺	-4.5	-5.5	+2.0	-3.2	+3.0	-2.0	0.0
Fe ³⁺	-2.5	0.0	0.0	-0.8	-0.5	+1.2	-5.0
Co ²⁺	-6.0	+1.5	-2.0	-3.8	-3.0	-2.0	-7.0
Ni ²⁺	-5.5	-2.0	-4.0	-6.0	-2.8	-3.0	-6.5
Cu ²⁺	-3.0	0.0	+2.5	-0.3	-1.0	+3.0	-6.0
Zn ²⁺	-7.0	+4.0	+2.8	-2.7	+2.2	+3.0	-3.2
Zr ⁴⁺	-0.5	-3.0	-0.5	-1.5	+2.0	-4.0	0.0
Nb ⁵⁺	-4.5	+4.8	-6.0	0.0	0.0	-2.8	0.0
Mo ⁶⁺	0.0	0.0	-1.5	0.0	0.0	+1.5	0.0
Rh ³⁺	-7.8	+6.0	-2.8	-4.5	-4.5	+6.0	0.0
Pd ²⁺	+3.0	-2.5	0.0	-1.8	+1.0	-5.5	+2.0
Ag ⁺	-4.7	-1.5	0.0	-0.8	-1.0	-4.0	-3.2
Cd ²⁺	-6.7	0.0	-4.0	-2.0	-7.5	-6.5	-1.8
La ³⁺	-6.2	-3.4	-1.4	+3.5	+1.8	+2.5	-6.0
Ta ⁵⁺	-2.0	-3.0	-1.5	-2.0	0.0	-3.8	0.0
W ⁶⁺	N.D.	0.0	-1.5	-0.5	0.0	0.0	0.0
Pt ⁴⁺	+3.0	+3.0	-3.0	0.0	0.0	0.0	+2.5
Au ³⁺	0.0	0.0	-1.5	+1.0	+1.0	+4.0	0.0
Hg ²⁺	0.0	0.0	0.0	-3.0	+2.0	+4.5	0.0
Hg ₂ ²⁺	-2.5	+2.0	-2.0	+2.0	+1.6	-2.5	-1.0
Th ⁴⁺	-4.0	-3.0	-1.5	0.0	+1.0	+0.8	-5.5
UO ₂ ²⁺	-3.0	0.0	-1.0	-0.8	-1.8	+1.5	-3.5

N.D. - Not detected

TABLE II

PRECIPITATION OF CATIONS FROM SOLUTION AFTER THE ADDITION OF
BACK-GROUND ELECTROLYTE

Background electrolyte	Cations which precipitate	Cations which do not precipitate
S I	Au^{3+} and Mo^{6+}	Hg_2^{2+} , Zr^{4+}
S II	None	Hg^{2+} , Cd^{2+} , VO_2^{2+} , Fe^{3+} , Cr^{3+} , Cu^{2+} , W^{6+} , Mo^{6+} and Au^{3+}
S III	Ag^+ and Fe^{3+}	Hg_2^{2+} , Pd^{2+} , Cr^{3+} and Zr^{4+} .
S IV	Th^{4+}	Pt^{4+} , Nb^{5+} & Mo^{6+} .
S V	None	Fe^{3+} , W^{6+} , Mo^{6+} , Pt^{4+} , Nb^{5+} , Ta^{5+} .
S VI	W^{6+}	Pt^{4+} .

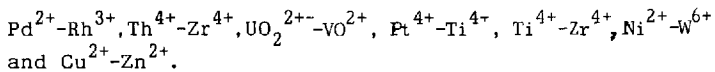
electrolyte was added to the cation solution. A number of ions precipitated under these conditions (TABLE II). In such cases, the precipitation mechanism also holds good.

- (3) To study the complexation effect ionophoresis was also performed in HNO_3 (0.1M). In most cases there is a decrease in migration due to complex formation eg. Hg^{2+} , Pd^{2+} , Ni^{2+} , Mn^{2+} , Pt^{4+} , La^{3+} , Nb^{5+} , Ta^{5+} & Zr^{4+} .
- (4) Heating effect is noticed when ionophoresis for some cations was performed at 400 volts for 30 min. and 1 h. A temperature increase

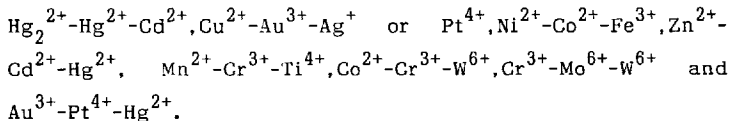
of 4° and 5° respectively is noted which may cause suction effect enabling the electrolyte flow from the sides towards the centre of the coated plate. To avoid the suction effect, the electrophoretic studies were carried out at 100 Volts for 3 h causing no significant change in temperature.

The complexing ability of the background electrolytes led to some very useful separations on silica gel-G layers. In order to see whether Pd^{2+} and Pt^{4+} can be successfully separated from numerous metal ions in 0.1M Oxalic acid as back-ground electrolyte, some binary mixtures of Pd^{2+} and Pt^{4+} with other metal ions were tried and as a result Pd^{2+} and Pt^{4+} were separated from Ti^{4+} , VO_2^{2+} , Cr^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Zr^{4+} , Nb^{5+} , Mo^{6+} , Rh^{3+} , Ag^+ , Cd^{2+} , La^{3+} , Ta^{5+} , W^{6+} , Au^{3+} , Hg_2^{2+} , Hg^{2+} , Th^{4+} and UO_2^{2+} . As a result of opposite or differential migration of cations a large number of binary and ternary separations were possible. Some of the important metal ion separations actually achieved on these layers are:

(i) Binary Separations:



(ii) Ternary Separations:



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