

**ELECTROPHORETIC STUDIES OF METAL IONS
AND ANIONS ON ZIRCONIUM(IV)
PHENYLETHYLAMINE-IMPREGNATED PAPERS**

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SUMMARY

The electrophoretic behaviour of some metal ions and anions has been studied on Whatman No. 1 paper strips impregnated with zirconium(IV) phenylethylamine; acetate buffers of different pH were used as background electrolytes. The effect of the ion-exchange material on the mobility of the ionic species was examined. It was found that impregnation of the paper with zirconium(IV) phenylethylamine enhances its separation potential. On the basis of the different migration of the ionic species several important binary and ternary separations have been achieved with acetate buffer systems.

INTRODUCTION

Synthetic inorganic ion exchangers have attracted attention because of their versatility in separation science and in many other different fields [1–9]. Chromatography on paper impregnated with inorganic ion exchangers has been found useful in the separation of cations and anions. The improved results can be attributed to selective ion exchange, adsorption behaviour, or a combination of these. Chromatographic papers impregnated with inorganic ion exchangers have been used in electrophoretic studies of metal ions – in which application of electric potential results in more favourable separating conditions [10–14].

Although zirconium(IV) phenylethylamine has promising characteristics as an anion exchanger and has been used in column chromatography of anionic species [15], systematic electrochromatographic study of metal ions and anionic species on paper impregnated with zirconium (IV) phenylethylamine is still lacking. This communication, therefore, describes the electrophoretic behaviour of metal ions and anionic species

on Whatman No. 1 paper impregnated with zirconium(IV) phenylethylamine, with acetate buffer of pH from 2 to 5 as background electrolyte.

EXPERIMENTAL

Reagents

Phenylethylamine (Eastman Kodak, USA) and zirconium oxychloride (BDH) were used for preparation of ion-exchange papers. Other chemicals were analytical reagent grade.

Apparatus

Electrophoretic studies were performed on horizontal 30 cm × 5 cm Whatman No. 1 paper strips in an apparatus connected to a regulated power supply (Hindustan Tronix model EPH-510).

Preparation of Zirconium(IV) Phenylethylamine-Impregnated Papers

The paper strips were dipped in aqueous Zr(IV) oxychloride solution (0.10 M) for a few seconds. After drying on filter paper the strips were dipped in an alcoholic solution of phenylethylamine (0.10 M) for a few seconds and dried again at room temperature. Excess reagents were removed by washing with distilled water and the strips were finally dried and used in this form.

Test Solutions

The anion solutions were 0.10 M aqueous solutions of the sodium, potassium, or ammonium salts of the anions under investigation. The cation solutions were 0.10 M aqueous solutions of chlorides, nitrates, or sulphates of the metals of interest. A 0.10 M solution of mercuric nitrate in 0.50 M HNO₃ and a 0.10 M solution of ceric ammonium sulphate in 1.8 M H₂SO₄ were also prepared.

Background Electrolytes

Four background electrolytes of pH 2.0, 3.0, 4.0, and 5.0 were prepared by mixing appropriate volumes of 1.0 M CH₃COOH and 1.0 M HCl solutions.

Detection of Anions

A 1.0% ethanolic solution of diphenylcarbazide was used for detection of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$, a 4.5% solution of ammonium molybdate in HNO_3 for detection of PO_4^{3-} and AsO_4^{3-} , a 4.0% solution of FeCl_3 in 0.01 M HCl for detection of SCN^- and $\text{Fe}(\text{SCN})_6^{4-}$, a 4.0% solution of FeSO_4 in 0.01 M H_2SO_4 for detection of $\text{Fe}(\text{SCN})_6^{3-}$, a 0.10 M solution of SnCl_2 in 4 M HCl for detection of WO_4^{2-} , a 20% solution of H_2SO_4 containing 1.0% H_2O_2 for detection of VO_3^- , and a 5% solution of SnCl_2 in 3 M HCl containing 10% KSCN for detection of MoO_4^{2-} .

Detection of Cations

A 2.0% aqueous solution of sodium sulphide was used for detection of Ag^+ , Pb^{2+} , Hg^{2+} , Cd^{2+} , Bi^{3+} , As^{3+} , and Sb^{3+} , a 0.1% alcoholic solution of alizarin red-S for detection of Ce^{4+} and Th^{4+} , a 1.0% aqueous solution of $\text{K}_4\text{Fe}(\text{CN})_6$ for detection of Cu^{2+} , a 0.1% aqueous aluminon solution for detection of Al^{3+} , and a 1.0% alcoholic solution of diphenylcarbazide for detection of Zn^{2+} , UO_2^{2+} , and Fe^{3+} .

Procedure

The electrophoresis chambers were filled with background electrolyte and the paper strips were placed horizontally on a suitable support. After conditioning of the paper strips a small drop of test solution was applied at the centre of each strip by means of a thin glass capillary. Electrophoresis was performed for 1 h at 220 V and 20 mA. After development the strips were dried in an oven at 60°C. The positions of the ionic species were detected by spraying with appropriate reagent. Migration of ions toward the anode or cathode was determined by measuring the distance of the middle of the spot from the point of application.

RESULTS AND DISCUSSION

The electrophoretic behaviour of some cations and anions was studied on zirconium(IV) phenylethylamine-impregnated paper and on unmodified Whatman No. 1 paper, with sodium acetate– HCl buffers of different pH as background electrolytes. The results obtained are shown in Tables I and II. The mobility of the ions on impregnated papers under the action of an applied potential depends on the size and charge of components,

the relative masses of the ionic species, adsorption on the ion exchanger, and on the nature of the background electrolyte.

Table I

Electrophoretic movement (cm) of anions on papers impregnated with zirconium(IV) phenylethylamine, with acetate buffers (1.0 M CH₃COONa–1.0 M HCl) of different pH as background electrolytes

Anion	pH 2	pH 3	pH 4	pH 5
SCN ⁻	3.90 (4.40)	1.70 (4.40)	1.90 (4.00)	2.30 (4.03)
VO ₃ ⁻	0.00 (2.00)	0.00 (2.90)	0.00 (6.00)	0.00 (5.30)
CrO ₄ ²⁻	0.50 (1.80)	1.20 (2.60)	1.50 (4.10)	1.60 (3.60)
Cr ₂ O ₇ ²⁻	0.80 (1.90)	0.90 (2.80)	1.00 (3.00)	1.00 (3.90)
MoO ₄ ²⁻	0.00 (1.10)	0.00 (1.50)	0.00 (1.80)	0.00 (2.00)
AsO ₄ ³⁻	0.00 (0.00)	0.00 (1.90)	0.00 (3.20)	0.00 (2.80)
PO ₄ ³⁻	0.00 (0.00)	0.00 (2.10)	0.00 (3.40)	0.00 (2.20)
Fe(CN) ₆ ³⁻	3.40 (4.30)	3.50 (4.70)	4.90 (7.10)	2.00 (3.10)
Fe(CN) ₆ ⁴⁻	2.20 (4.00)	3.20 (4.20)	5.60 (6.30)	1.50 (4.90)

Figures in parentheses show the movement of the ions on untreated papers

Zirconium(IV) phenylethylamine behaves as an anion exchanger and its ion-exchange capacity decreases with increasing pH of the external solution [15]. The migration of Fe(CN)₆³⁻, Fe(CN)₆⁴⁻, CrO₄²⁻, and Cr₂O₇²⁻ increases as electrolyte pH is increased from 2; that of Fe(CN)₆³⁻ and Fe(CN)₆⁴⁻ decreases at pH > 4.0. The slow movement of ions at lower pH might be because of the ion-exchange phenomenon. It is apparent from Table I that AsO₄³⁻, PO₄³⁻, MoO₄²⁻, and VO₃⁻ do not move from the point of application on impregnated paper whereas movement of these ions is recorded on the untreated papers. This is possibly because of adsorption of these species on the impregnated papers. On the basis of differences between the migration of the anions several binary and ternary separations were achieved on impregnated papers. These are listed in Table III.

It is apparent from Table II that Cu²⁺, VO²⁺, Al³⁺, and Bi³⁺ did not move in the pH range 2 to 4, but moved toward the anode at pH 5. Ag⁺ remained at the point of application in all the systems studied. Cd²⁺ and Fe³⁺ moved toward the anode at pH < 4. In a similar fashion Hg²⁺ also interacts with the background electrolyte in the pH range 2–4, forming a negative species which moved toward the anode.

Table II

Electrophoretic movement (cm) of metal ions on paper impregnated with zirconium(IV) phenylethylamine, with acetate buffers (1.0 M CH₃COONa–1.0 M HCl) of different pH as background electrolytes

Metal ion	pH 2	pH 3	pH 4	pH 5
Ag ⁺	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Pb ²⁺	-1.20 (-1.80)	-1.10 (-1.50)	-0.80 (-1.30)	-1.60 (-2.90)
Hg ²⁺	2.20 (+3.50)	2.20 (+2.80)	2.60 (+2.80)	-1.10 (-1.20)
Cd ²⁺	-0.60 (-1.50)	-1.40 (-1.90)	6.10 (+6.90)	0.70 (-1.10)
Cu ²⁺	0.00 (0.00)	0.00 (-0.90)	0.00 (-0.80)	-0.90 (-4.20)
Zn ²⁺	-2.20 (-2.55)	-2.00 (-2.35)	-1.20 (-1.70)	-1.80 (2.20)
VO ²⁺	0.00 (-1.70)	0.00 (-1.90)	0.00 (-1.50)	-0.60 (-1.30)
UO ₂ ²⁺	-1.50 (-1.90)	-1.50 (-2.30)	-1.90 (-2.10)	-1.70 (-1.60)
Al ³⁺	0.00 (0.00)	0.00 (0.00)	0.00 (-2.90)	-0.60 (-2.30)
Fe ³⁺	-0.60 (-3.40)	-0.60 (-1.60)	1.50 (+1.60)	2.50 (+3.20)
Bi ³⁺	0.00 (-1.30)	0.00 (0.00)	0.00 (0.00)	-1.60 (-2.00)
Th ⁴⁺	-0.30 (-1.80)	-0.40 (-1.10)	-1.10 (-1.70)	-1.20 (-2.20)
Ce ⁴⁺	-5.05 (-8.50)	-1.05 (-2.10)	0.00 (-0.90)	-1.10 (-1.90)

Figures in parentheses show the movement of the ions on untreated papers. Negative signs indicate movement toward the anode, otherwise movement is toward the cathode

The results reported in Table II reveal that several analytically important separations of metal ions which could not be achieved on untreated papers should be possible on impregnated papers. These include: at pH 2, Pb²⁺–Cd²⁺–VO²⁺; Pb²⁺–Bi²⁺–VO²⁺; and Pb²⁺–Th⁴⁺; at pH 3, Pb²⁺–Zd²⁺–VO²⁺; Pb²⁺–Fe³⁺; Cd²⁺–VO²⁺; and Zn²⁺–UO₃²⁺; and at pH 5, Zn²⁺–VO²⁺; Zn²⁺–Al³⁺; Th⁴⁺–VO²⁺; Bi³⁺–Al³⁺; and Bi³⁺–VO²⁺. Electrochromatography on Zr(IV) phenylethylamine papers was found to be suitable for the separation of many cations of analytical importance. Some of these separations are listed in Table IV.

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Table III

Anion separations achieved on zirconium(IV) phenylethylamine-impregnated papers by use of acetate buffers (1.0 M CH₃COONa–1.0 M HCl) of different pH as background electrolytes

pH	No.	Separation
2	1	CrO ₄ ²⁻ (0.60)–Fe(CN) ₆ ⁴⁻ (2.20)–SCN ⁻ (3.90)
	2	VO ₃ ⁻ (0.00)–Cr ₂ O ₇ ²⁻ (0.80)–Fe(CN) ₆ ³⁻ (3.40)
	3	Cr ₂ O ₇ ²⁻ (0.80)–Fe(CN) ₆ ⁴⁻ (2.20)–Fe(CN) ₆ ³⁻ (3.50)
	4	Cr ₂ O ₇ ²⁻ (0.80)–Fe(CN) ₆ ⁴⁻ (2.20)–SCN ⁻ (3.80)
3	1	MoO ₄ ²⁻ (0.00)–SCN ⁻ (1.70)–Fe(CN) ₆ ⁴⁻ (3.20)
	2	MoO ₄ ³⁻ (0.00)–SCN ⁻ (1.60)–Fe(CN) ₆ ⁴⁻ (3.10)
	3	VO ₃ ⁻ (0.00)–Cr ₂ O ₇ ²⁻ (0.90)–Fe(CN) ₆ ³⁻ (3.40)
	4	VO ₃ ⁻ (0.00)–SCN ⁻ (1.70)–Fe(CN) ₆ ³⁻ (3.40)
4	1	VO ₃ ⁻ (0.00)–SCN ⁻ (1.90)–Fe(CN) ₆ ⁴⁻ (5.60)
	2	VO ₃ ⁻ (0.00)–Cr ₂ O ₇ ²⁻ (1.00)–Fe(CN) ₆ ³⁻ (4.80)
	3	MoO ₄ ²⁻ (0.00)–SCN ⁻ (1.80)–Fe(CN) ₆ ³⁻ (4.90)
5	1	MoO ₄ ²⁻ (0.00)–Fe(CN) ₆ ⁴⁻ (1.50)
	2	MoO ₄ ²⁻ (0.00)–SCN ⁻ (2.03)
	3	VO ₃ ⁻ (0.00)–CrO ₄ ²⁻ (1.50)
	4	VO ₃ ⁻ (0.00)–Fe(CN) ₆ ³⁻ (1.90)

Table IV

Separations of metal ions achieved on papers impregnated with Zr(IV) phenylethylamine by electrochromatography with acetate buffer (1.0 M CH₃COONa–1.0 M HCl) of pH 4 as background electrolyte

No.	Separation
1	UO ₂ ²⁺ (-1.90)–Ag ⁺ (0.00)–Cd ²⁺ (+6.10)
2	Th ⁴⁺ (-1.10)–Ag ⁺ (0.00)–Cd ²⁺ (+6.00)
3	Pb ²⁺ (-0.80)–Ag ⁺ (0.00)–Cd ²⁺ (+6.00)
4	Fe ³⁺ (+1.55)–Ag ⁺ (0.00)–Cd ²⁺ (+6.10)
5	Pb ²⁺ (-0.70)–Ag ⁺ (0.00)–Fe ³⁺ (+1.60)
6	Pb ²⁺ (-0.90)–Ag ⁺ (0.00)–Hg ²⁺ (+2.60)
7	UO ₂ ²⁺ (-1.80)–Ag ⁺ (0.00)–Hg ²⁺ (+2.50)
8	Th ⁴⁺ (-1.20)–Ag ⁺ (0.00)–Fe ³⁺ (+1.50)

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