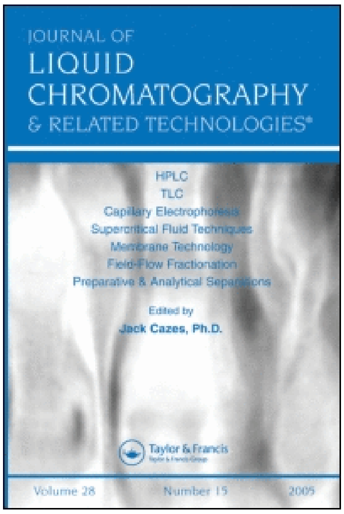

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ELECTROCHROMATOGRAPHY OF METAL IONS ON ZIRCONIUM(IV) PHOSPHOANTIMONATE PAPERS: QUANTITATIVE SEPARATION OF PLATINUM(IV) FROM PLATINUM GROUP AND OTHER METAL IONS†

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ABSTRACT

Zirconium(IV) phosphoantimonate impregnated papers have been used to study the electrochromatographic behaviour of 29 metal ions in buffers of weak organic acids with their corresponding ammonium salts as background electrolytes at fixed voltage and time intervals. As a result of these investigations, the variation in the average mobility of metal ions with the ionisation constants of the organic acids used in buffers and other parameters such as atomic numbers and charge on the metal ions has been studied. On the basis of the differential mobilites of the metal ions, which depends on the ion exchange properties of Zr(IV) phosphoantimonate and the nature of the complexes formed with the electrolytes, some binary, ternary and quarternary separation have been achieved. Besides microgram separations (25 µg-100 µg) of Pt(IV) from Pt group and other metal ions have also been achieved.

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INTRODUCTION

Electrochromatographic studies of metal ions on papers impregnated with antimonate ion exchangers have been reported from our laboratories and some useful, analytically difficult and highly selective separations of cations in binary and multicomponent mixtures have been achieved[1-3].Most of the work has been carried out on single salts and on hydrous oxides of poly-valent metals[4-6]. However, a scarce attention has been paid to use the double salts in paper electrochromatography yet. Zirconium (IV) phosphoantimonate shows high chemical stability and good ion exchange capacity (1.86 meq/dry gm) compared to their parent single salts because such salts possess the combined properties of both the single salts, and other antimonate ion exchangers. It has been proved useful in thin layer[7], paper, and column chromatography[8]. All these results have given us impetus to extend our work on electrochromatographic studies of metal ions on Zr(IV) phosphoantimonate impregnated papers.

It is also evident from the available literature on electrochromatography which covers the papers upto 1989, that the simple aqueous systems have been mostly choosen as background electrolyte. No attemp appears to have been made to use the buffer mixtures of weak organic acids and their corresponding ammonium salts as background electrolyte. Hence, the present studies have, therefore, been undertaken to study the electrochromatographic behaviour of metal ions on papers impregnated with Zirconium (IV) phosphoantimonate using buffers of organic acids with their corresponding ammonium salts as back ground electrolyte. During these investigations, the variations in average mobility of metal ions with ionisatin constants of the acids used in buffers and with other parameters such as atomic numbers and charge on the metal ions has been studied. On the basis of differential mobility of metal ions, a large number of analytically important separations of binary, ternary and multicomponent mixtures of inorganic ions have been achieved. The unique feature of these studies has been the separation of Pt(IV) from its group metals. Besides a rapid quantitative separatin of Pt(IV) (25 µg-100 µg) from binary, ternary and multicomponent mixtures of cations has been achieved on Zr(IV) phosphoantimonate papers by using buffer of acetic acid and ammonium acetate as background electrolyte. The method has proved to be useful for the separation of platinum from Rasin and terpentine industry, fertilizer and chemical industry waste water, where platinum is used as catalyst.

EXPERIMENTAL

Apparatus

The electphoretic studies were performed on whatman No.1 strips of 46.4x.75 cm. A horizontal type electrophoresis apparatus run on electronically regulated power supply unit (Systronics Ltd., India)was used, spectrophotometric studies were made using a Bausch and Lomb spectronic 20, colorimeter.

Reagents and Chemicals

Pure laboratory reagent grade chemicals and solvents from B.D.H., S.M., E. Merck and Hopkin and Williams (England) were used for these studies.

Test solutions and detection reagents

For the qualitative studies, cation solutions and detectors were prepared and used as described earlier(1). For quantitative studies a stock solution of Pt(IV) (10,000 ppm Pt) was prepared.

Background electrolyte solutions:

The following six mixed background electrolyte solutions were used in these studies:

(i) 0.1 M Formic acid + 0.1 M Ammonium formate (1:1)

(ii) 0.1 M Acetic acid + 0.1 M Ammonium acetate (1:1)

(iii) 0.1 M Lactic acid + 0.1 M Ammonium lactate (1:1)

(iv) 0.1 M Oxalic acid + 0.1 M Ammonium oxalate (1:1)

(v) 0.1 M Tartaric acid + 0.1 M Ammonium tartarate (1:1)

(vi) 0.1 M Citric acid + 0.1 M Ammonium citrate (1:1)

Procedure

For qualitative studies on electrophoretic migration, the earlier method[3] was followed.

In quantitative work, the platinum solution (25 µg-100 µg) along with the cations to be separated were applied on the strips with the help of a "Lambda pipette". The strips were electrochromatographed in acetic acid and ammonium acetate buffer solution for three hours under a potential of 200 V. After the required time the pilot strips were examined for the spots of platinum and other cations. The remaining strips were then cut according to where spots had appeared on the pilot strips and platinum was eluted with 40 ml of 10% HCl in the cold by using 20 ml twice. The strips than washed with 20 ml of D.M.W. The solution was evaporated to small volumes (2-3 ml) and the paper strips were oxidised with an oxidising mixture of HClO: HNO_3: H_2SO_4 in ratio of 3:1:4. The solution was filtered off, evaporated to dryness and extracted with deionised water.

The blank was run in a similar way following the entire procedure with unspotted strip. Zirconium phosphoantimonate ion exchanger on the strips which remained undisolved was filtered off. Platinum was determined spectrophotometrically with the stannous chloride method[9].

RESULTS

The electrophoretic migration distances (in cm) of 29 metal ions in all the above background electrolyte solutions were measured. On the basis of differences in migration distances and the direction of movement of cations, several important and analytically difficult binary, ternary and quarternary separation have been possible, some of which are listed in Table 1. Results of quantitative studies are summarised in Table 2 and 3.

DISCUSSION

The background electrolyte no. 1 to 6 are all buffer solutions obtained by mixing weak organic acids with their corresponding ammonium salts. It is observed that these buffer systems produce a higher mobility of metal ions as compared with single aqueous acids. Mobilities of metal ions are found to increase with the increase in ionisation constants of acids used in the buffers. The order of increase in ionisation constants of acids being acetic acid ($1.8\text{x}10^{-5}$)$<$lactic acid ($13.87\text{x}10^{5}$)$<$formic acid ($17.7\text{x}10^{-5}$)$<$citric acid ($87 \text{ x } 10^{-5}$)$<$tartric acid ($96\text{x}10^{-5}$) oxalic)$<$Oxalic acid ($6500 \text{ x } 10^{-5}$) and the order of average mobility of all metal ions in these electrolytes is also found to be the same. This increase in mobility with the ionisation constants of acids is probably due to the increase in the number of available H^+ ions competing with the metal ions in the exchange process. It is also inferred from migration distances that the average mobility of metal ions is positive in buffer mixtures of polybasic acid, the first ionisation constants of which vary from $87 \text{ x } 10^{-5}$ to $6500 \text{ x } 10^{-5}$. This behaviour may be due to the formation of anionic complexes by a majority of metal ions.

Figure 1 depicts the variations of average mobility of all the metal ions with the ionisation constants of acids used in buffer solutions used as background electrolytes. Barring formic acid, all other acids produce high mobility of metal ions which continuously increase with the ionisation constants of acids as explained above. The average mobility is also found to increase with increase in atomic no. for most of the metal ions. Besides,

TABLE - 1

Separation Achieved on Zirconium (IV) Phospho-Antimonate papers.

Background Electrolyte	Metal ion separations
0.1M	Bi^{3+}(0.0) - Pb^{2+}(-3.1) - Cd^{2+} (-6.3)
Formic Acid	Bi^{3+}(0.0) - Pb^{2+}(-3.1)- Hg^{2+}(+4.1)
+	Zn^{2+}(-9.7))- Cd^{2+} (-6.3) - Hg^{2+} (+4.1)
0.1M	Y^{3+}(-8.7) - Zr^{4+}(0.0) - Th^{4+}(-2.9)
Ammonium formate	Zn^{2+} (-9.6) - Fe^{3+}(-2.8)
	Cr^{3+} (-8.6) - Fe^{3+} (-2.7)
	Zr^{4+}(0.0) - Th^{4+} (-2.9)
0.1M	Ru^{3+}(-2.0)-Au^{3+}(0.0) - Ir^{+3}(+3.1) - Pt 4^{+}(+9.0)
Acetic Acid +	Y^{3+}(-7.0) - Zr^{4+} (0.0)/Th^{4+}(-1.2)-Ir^{3+}(+3.1)
+	Au^{3+}(0.0)- Cu^{2+}(-5.8)-Ni^{2+}(-8.1)
0.1M	Co^{2+}(-6.4)-Ni^{2+}(-8.1)
Ammonium Acetate	Cu^{2+}(-5.8)-Ni^{2+}(-8.0)
(1:1)	
0.1M	Fe^{3+}(-2.1) - Se^{4+} (+3.0) - Pt^{4+}(+8.7)
Lactic Acid	W^{6+}(0.0) - Se^{4+} (+3.0) - Pt^{4+}(+8.8)
+	W^{6+}(0.0) - Se^{4+}(+3.0) - Pt^{4+}(+8.8)
0.1M	Th^{4+}(-1.4) - Y^{3+}(-7.4)
Ammonium Lactate	Ir^{3+}(+2.8)-Ru^{3+}(-4.0)
(1:1)	Zn^{2+}(-8.7)-Pb^{2+}(-3.4)
	Ag^{+}(0.0) - Au^{3+}(+6.0)
0.1M	Se^{4+}(+3.5) - W^{6+} (+6.5)-Cu^{2+}(-7.5)
Oxalic Acid	Pb^{2+}(0.0) - Hg^{2+} (+4.5)
+	Bi^{3+}(0.0) - Hg^{2+}(+4.5)
0.1M	Fe^{3+}(0.0) - MO^{6+}(+6.8)
Ammonium Oxalate	Fe^{3+}(0.0) - W^{6+} (+6.5)
(1:1)	
0.1M	Bi^{3+}(0.0) -Zn^{2+}(-4 .1)-Cd^{2+}(-8.2)
Tartaric Acid	Bi^{3+}(0.0) - W^{6+}(+7.8)
+	Bi^{3+}(0.0) - Mo^{6+}(+5.7)

Contd...

TABLE 1 (continued)

Background Electrolyte	Metal ion separation
0.1M	Ni^{2+}(-5.2) - Bi^{3+}[0·0]
Ammonium Tartarate	
(1:1)	
0.1M	Pt^{4+}(+6.5) - Ru^{3+}(-3.5)-Ir^{3+}(+2.2)
Citric Acid	Zn^{2+} (-7.4) - Mn^{2+}(+0.5)
+	Pb^{2+}(-0.9) - Cd^{2+}(-7.8)
0.1M	Cr^{3+}(-4.1) - Fe^{3+}(-7.4)
Ammonium Citrate	$Ag.^{+}$(0.0) - Pt^{4+}(+6.5)
(1:1)	

the average mobility decreases with the increase in charge on the metal ions. The utility of Zr(IV) phospho antimonate papers in electrochromatography is demonstrated by achieving a large number of useful separations (Table 1). Several important and analytically difficult, ternary and binary separation of metal ions have been achieved. To mention a few Zr^{4+}-Pt^{4+}, Ir^{3+}-Pt^{4+}, Cr^{3}-Fe^{3+}, Ir^{3+}-Ru^{3+}, Zn^{2+}-Pb^{2+}, Bi^{3+}-Hg^{2+}, Th^{4+}-Pt^{4+}, Bi^{3+}-Zn^{2+}-Cd^{2+}, Pt^{4+}-Ru^{3+}-Ir^{3+}, Fe^{3+}-Ni^{2+}-Pt^{4+}, Au^{3+}-Ir^{3+}-Pt^{4+}, etc. are separations of analytical interest.

The unique feature of these studies has been the quantitative separations of Pt^{4+} from metals of platinum group and other metals. This is probably due to the fact that Pt^{4+} forms anionic complex in most of the background electrolytes which results in high mobility of Pt^{4+} ion towards anode. The results of these studies have been summarized in Table 2 and 3. While binary and ternary separtions of Pt^{4+} from synthetic mixtures of ther metals have been given in Table 2, the quantitative estimation of Pt^{4+} from multicomponent mixtures containing platinum

TABLE - 2

Quantitative Separation of Platinum from Binary and ternary mixtures

(i) Amount of platinum applied on each strip - 50 µg

(ii) Solvent system-0.1M Acetic acid +0.1M Ammonium acetate (1:1)

(iii) Potential - 200 volts

(iv) Time-3 hrs

Metal ions mixture	Amount of Pt found (µg)	% error
1. W^{6+} - Pt^{4+}	46	- 8
2. Ni^{2+} - Pt^{4+}	54	+ 8
3. CO^{2+} - Pt^{4+}	49	- 2
4. Fe^{3+} - Pt^{4+}	46	- 8
5. Au^{3+} - Pt^{4+}	53	+ 6
6. Ir^{3+} - Pt^{4+}	48	- 4
7. Ru^{3+} - Pt^{4+}	54	+ 8
8. Zr^{4+} - Pt^{4}	47	- 6
9. Th^{4+} - Pt^{4+}	46	- 8
10. Fe^{3+} - Co^{2+} - Pt^{4+}	48	- 4
11. Fe^{3+} - Ni^{2+} - Pt^{4+}	48	- 4
12. Co^{2+} - Ni^{3+} - Pt^{4+}	47	- 6
13. Au^{3+} - Ir^{3+} - Pt^{4+}	51	+ 2
14. Zr^{4+} - Ir^{3+} - Pt^{4+}	47	- 6
15. Y^{3+} - Ir^{3+} - Pt^{4+}	49	- 2

TABLE 3

Quantitative separation of Platinum from Multicomponent Mixtures

(i) Solvent system -0.1M Acetic acid +0.1M Ammonium acetate (1:1)
(ii) Potential - 200 V.
(iii) Time-3 hrs

Composition of mixture	Amount of Pt^{4+} applied (µg)	Amout of $Pt^{4}+$ found (µg)	% Error
10 µl each of 10^{-1}M solution of Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+} Cd^{2+}, Ce^{3+}, Co^{2+}, Ni^{2+}, Pd^{2+}, Zn^{2+}, Fe^{3+}, Ir^{3+}, Ru^{3+}, Zr^{4+}, Th^{4+},Au^{3+} and W^{6+} mixed with 25 µg to 100 µg Pt^{4+}	25	23	-8.0
	25	24	-4.0
	40	38	-5.0
	40	40	-0.0
	50	52	+4.0
	50	47	-6.0
	60	59	-1.6
	60	58	-3.3
	80	82	+2.4
	80	76	-5.0
	100	99	-1.0
	100	104	+4.0

group metals and other metals have been shown in Table 3. The microgram estimation of Pt^{4+} (50 µg in case of binary and ternary mixtures and 25 µg to 100 µg in case of mixtures containing several ions) was done as per the literature method[9]. The results are found to be quite accurate and reproducible.

The method can be applied for the separation of platinum from industrial effluent of rasin and terpentine industry, chemical and fertilizer industry waste water, where platinum is used as catalyst.

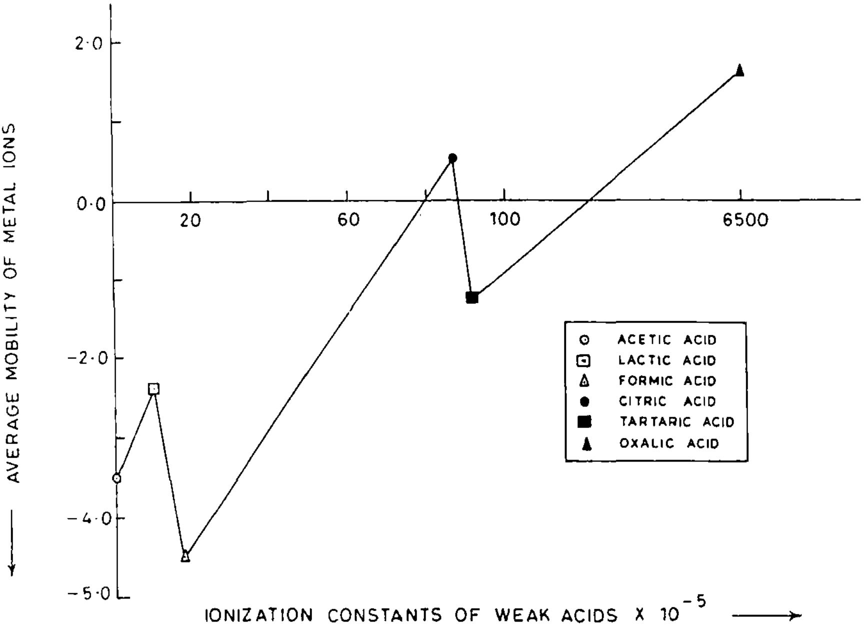

FIG. 1 AVERAGE MOBILITY OF METAL IONS ON ZIRCONIUM (IV) PHOSPHOANTIMONATE PAPERS VS. IONIZATION CONSTANTS OF WEAK ACIDS

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