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CAPILLARY-TUBE ISOTACHOPHORETIC SEPARATION OF MOLYBDATE(VI), TUNGSTATE(VI) AND VANADATE(V) IONS USING ION-PAIRING EQUILIBRIA

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SUMMARY

The capillary-tube isotachopheresis technique has been used to separate molybdate(VI), tungstate(VI) and vanadate(V) ions. The ion-pairing equilibria between calcium ion and the above anions can be applied to improve the separation. A simultaneous separation can be achieved when the pH of the leading electrolyte containing calcium ion is 10.0. The separable range of these ions varies according to the concentration of calcium ion, the optimum concentration in the leading electrolyte being 2 mM. The relative standard deviations of simultaneous determinations were 1.0–2.5% at the 3.3 nmol level and the time required for the determination is only 20 min.

INTRODUCTION

Capillary-tube isotachopheresis (CITP) has many advantages such as the analysis time is short, no support or stationary phase is necessary and it is applicable to small amounts of sample. Many attempts have been made to improve the separability of CITP and it has been applied to a wide range of samples^{1–3}. We have also shown that complex-forming or ligand-replacement and/or dissociation equilibria are effective in improving the separability of CITP^{4–9}.

Few CITP investigations of the separation of metal oxo anions such as CrO_4^{2-} , MoO_4^{2-} and WO_4^{2-} have been reported¹⁰. Zolotov *et al.*¹¹ used ion chromatography to separate metal oxo anions. Liquid chromatography was used by Vespalet *et al.*¹². Thin-layer chromatography was used by Benes¹³ and Okumura and Nishikawa¹⁴ to separate anions. Taglia and Lederer¹⁵ demonstrated the separation of anions by isotachopheresis on filter-paper (paper electrophoresis). However, these methods have several disadvantages. Ion chromatography¹¹ of chromate ion resulted in a broad or tailing band. In liquid chromatography¹², vanadate ion is adsorbed on the column and cannot be eluted. For isotachopheresis¹⁵, a spacer ion, a concentrated sample solution and a long analytical time were required. In those methods, the support or stationary phase is essential. Its existence often brought about the undesirable adsorption of the sample anions. On the other hand, CITP not only does

not require a support, but it also would be an effective method to examine the interactions among the ions existing in the solution.

In the present work we have investigated the fundamental conditions for determination of metal oxo anions by CITP, such as the influence of the pH of the leading electrolyte, the effect of the counter ion for ion-pairing equilibria and the utility of the isotachophoretic zone length for obtaining information on the ionic species. A good separation of MoO_4^{2-} , WO_4^{2-} and HVO_4^{2-} (containing NO_3^- , CrO_4^{2-} or SO_4^{2-}) can be obtained by using ion-pairing equilibria.

EXPERIMENTAL

Apparatus

The isotachopherograms were obtained using a capillary tube isotachophoretic analyser Model IP-1B with a PGD-1 potential gradient detector (Shimadzu, Kyoto, Japan). The separation tube was 20 cm \times 0.5 mm I.D. Measurements of pH were made with an expanded-scale pH meter Model F-7ss (Horiba, Japan).

Materials

The stock solutions were prepared by dissolving the ammonium salts (molybdate and vanadate) and the sodium salt (tungstate) in twice distilled water. Standard solutions containing these three ions were made by mixing the individual stock solutions. The leading and terminating electrolyte systems are shown in Table I.

TABLE I
LEADING AND TERMINATING ELECTROLYTE SYSTEMS

Leading electrolyte*	pH	Driving current (μA)
(1) 0.01 M Cl^- + ϵ -aminocaproic acid	4.5	75
(2) 0.01 M Cl^- + creatinine	5.25	100
(3) 0.01 M Cl^- + histidine	5.5– 6.75	100
(4) 0.01 M Cl^- + Tris	7.0– 8.5	100
(5) 0.01 M Cl^- + ammonia	9.0–10.0	125
Terminating electrolyte	pH	
(6) 0.01 M Glutamic acid	3.5	
(7) 0.01 M TES** + Tris	7.5	
(8) 0.01 M β -Alanine + $\text{Ba}(\text{OH})_2$	10.6	

* 0.025% Poly(vinyl alcohol) (PVA) was added.

** N-Tris(hydroxymethyl)methyl-2-aminoethanesulphonic acid.

RESULTS AND DISCUSSION

Relationship between potential gradient ratio (PR) values⁹ and pH of the leading electrolyte

The migration behaviour of tungstate ion was very similar to that of molybdate ion. The PR values of tungstate and molybdate ions increased gradually with in-

creasing pH of the leading electrolyte, as shown in Fig. 1. It is difficult to separate tungstate and molybdate ion because they have similar effective mobilities and easily form a mixed zone. The PR values of vanadate ion are influenced not only by the pH of the leading electrolyte, but also by the type and concentration of buffer solution. When 2-amino-1,3-dihydroxy-2-hydroxymethylpropane(Tris) and an ammonium buffer were employed the PR values of vanadate ion tended to decrease with increasing pH. This is probably due to an increase in the interaction between the oxo anion and the constituent cation of the buffer, because much buffer reagent was required to raise the pH value of the solution. When histidine buffer was used, all of the PR values determined were smaller than that expected from the PR values of other buffer systems.

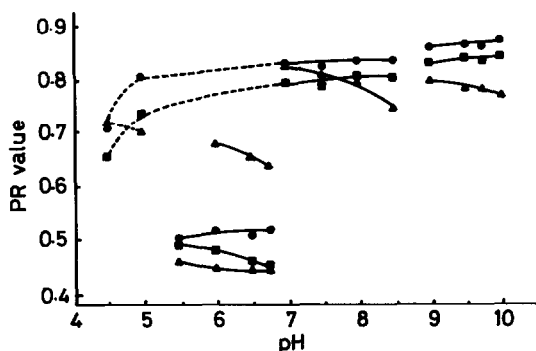


Fig. 1. Effect of pH of the leading electrolyte on the PR values of MoO_4^{2-} (●), WO_4^{2-} (■) and HVO_4^{2-} (▲). Conditions as in Table I.

In the range pH 6.0–6.8 of the leading electrolyte the vanadate ion shows two different PR values. This seems to be correlated with the number of species of vanadate ion existing under these conditions.

Zone length

The Kohlrausch function shows that the concentration of sample ion, C_{A-} , is determined by the concentration of the leading ion, C_{L-} , its mobility, U_{L-} , and charge, L_{L-} , the mobility of the counter ion, U_{R+} , the mobility of the sample ion U_{A-} and its charge, L_{A-} :

$$C_{A-} = C_{L-} U_{A-} (U_{L-} + U_{R+}) L_{L-} / U_{L-} (U_{A-} + U_{R+}) L_{A-}$$

The above equation indicates that the concentration of the sample ion is inversely proportional to its charge. Therefore, in CITP the zone length of the sample ion is proportional to the amount of sample ion and its charge.

The relationship between the zone length and the pH of the leading electrolyte is shown in Fig. 2. The zone length of molybdate ion was nearly constant and tended to decrease slightly at low pH. The zone length of tungstate ion increased rapidly in the range pH 5.5–6.5 and was constant at pH > 7.0. The zone length of vanadate ion, first increased between pH 5.5 and 6.0, then levelled off and finally increased again at pH > 8.0.

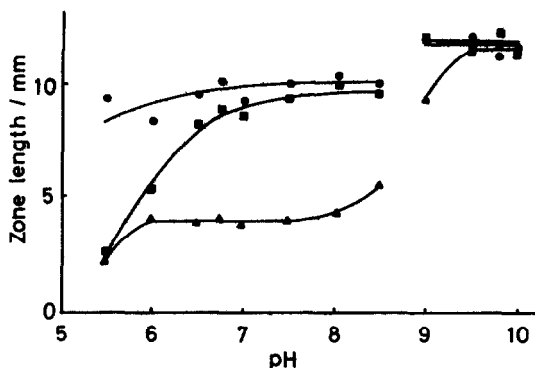


Fig. 2. Relationship between zone length and pH of the leading electrolyte. Conditions as in Table I. Ions as in Fig. 1.

The shortening in the zone length with decreasing pH shown in Fig. 2 suggests that a series of polymerization reactions of the metal oxo species may occur successively so as to decrease the charge per metal atom such as HVO_4^{2-} , $\text{V}_3\text{O}_3^{3-}$, $\text{V}_4\text{O}_{12}^{4-}$, $\text{HV}_{10}\text{O}_{28}^{5-}$, etc. Fig. 2 also shows that the tendency to polymerization increases in the order molybdate, tungstate and vanadate, in agreement with previous results^{16,17}. The difference between the zone length in Tris and the ammonium buffer system was due to the difference between the driving currents in these systems and in the mobilities of the buffer reagents. The mobility of histidine is nearly equal to that of Tris¹⁰. The driving currents in the histidine and Tris buffer systems were 100 μA in each case.

Effects of counter ions on PR value

The utility of the complex-forming or ion-pairing equilibria between molybdate, tungstate and vanadate and the counter ions was investigated by changing the counter ion as shown in Table II. The leading electrolytes containing 10 mM chloride ion and various amounts of a counter ion were adjusted to pH 10.0 with ammonia. The effective mobilities of the metal oxo anions did not change in the presence of caesium ion and tetraethylammonium ion (TEA^+). These cations are unfavourable

TABLE II

EFFECT OF COUNTER ION ON PR VALUE

Zeph^+ = Zephiramine cation; CTMA^+ = cetyltrimethylammonium; TEA^+ = tetraethylammonium.

	Without	1 mM			2 mM				
		Ca^{2+}	Zeph^+	CTMA^+	Ca^{2+}	Zeph^+	CTMA^+	Cs^+	TEA^+
MoO_4^{2-}	0.87	0.84	0.84	0.84	0.80	0.80	*	0.87	0.88
WO_4^{2-}	0.84	0.79	0.80	0.81	0.77	0.76	*	0.84	0.84
HVO_4^{2-}	0.77	0.72	0.69	0.65	0.67	0.43	*	0.78	0.78

* Not detectable.

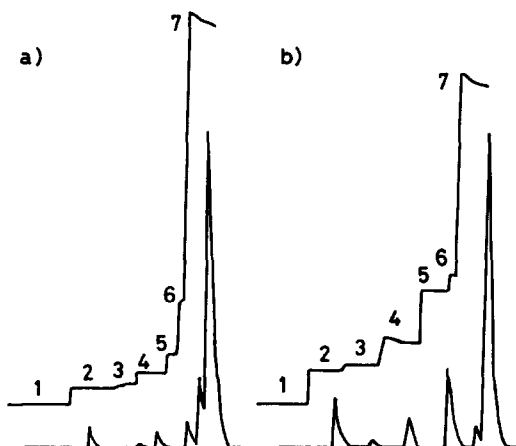


Fig. 3. Isotachopherograms without (a) and with 3 mM Ca^{2+} (b). Leading electrolyte: 0.01 M Cl^- , NH_3 , pH 10.0, 0.025% PVA. Migration current: 125 μA . Sample: 2.5 μl of a mixed solution of $1.7 \cdot 10^{-3}$ M. Zones: 1 = Cl^- ; 2 = MoO_4^{2-} ; 3 = WO_4^{2-} ; 4 = HVO_4^{2-} ; 5 = CO_3^{2-} ; 6 = HCO_3^- ; 7 = β -alanine.

as ion-pairing reagents. The presence of calcium ion, however, tends to decrease the PR values of molybdate(VI), tungstate(VI) and vanadate(V) ions, and the simultaneous separation of these three anions was achieved by the use of calcium ion as an ion-pairing reagent as shown in Fig. 3. The ionic radius of the quaternary ammonium ion is larger than those of calcium and caesium ions. However, the presence of TEA^+ had no influence on the PR values of the oxo ions. Larger ions than TEA^+ such as zephiramine and cetyltrimethylammonium ions tended to decrease the effective mobilities of the anions, as shown in Table II. In particular, the PR value of vanadate ion was greatly diminished by the presence of the latter cations. The PR values of molybdate and tungstate ions were also diminished by the addition of calcium ion, zephiramine or cetyltrimethylammonium ion. However when zephiramine or cetyltrimethylammonium ion was used as counter ion, the molybdate and tungstate ions easily formed a mixed zone and their separation was prevented.

The separable range of these oxo anions varies with the concentration of calcium ion in the leading electrolyte, as shown in Table III.

Effects of co-existing anions

The interference from co-existing anions was investigated at pH 10 using a leading electrolyte containing 2 mM calcium ion. The sample solutions were made by mixing equimolar amounts of molybdate, tungstate and vanadate and/or foreign anions (nitrate, chromate and/or sulphate ions).

TABLE III

EFFECT OF CALCIUM ION CONCENTRATION ON MAXIMUM SEPARABLE QUANTITY (nmol)

Concentration of Ca^{2+} (mM)	0	1	2	3	4
Sample (nmol)	3.3	4.2	7.0	5.0	4.2

TABLE IV

EFFECT OF CO-EXISTING ANIONS ON MAXIMUM SEPARABLE QUANTITY (nmol)

Co-existing anion (nmol)	None	NO_3^-	CrO_4^{2-}	SO_4^{2-}	All three anions
Sample (nmol)	7.0	6.3	5.0	4.4	4.2

Table IV shows the maximum separable quantity (nmol) of the sample metal oxo anions co-existing with the same quantity (nmol) of the above three foreign anions, individually or simultaneously. The separable quantities of the sample anions decrease with decreasing effective mobility of the co-existing anions, that is, in the order of NO_3^- , CrO_4^{2-} and SO_4^{2-} . The relative standard deviations of simultaneous determinations of the metal oxo anions were 1.0–2.5% at the 3.3 nmol level for five experiments.

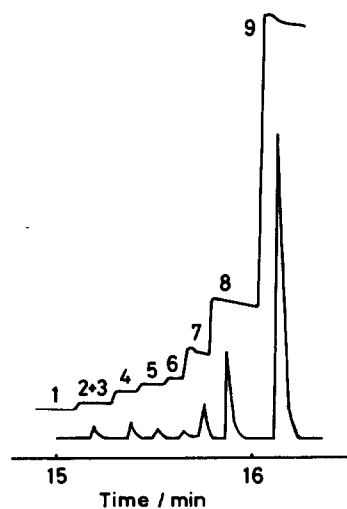


Fig. 4. Isotachopherogram in the presence of co-existing anions. Leading electrolyte: 0.01 M Cl^- , NH_3 , pH 10.0, 2 mM Ca^{2+} , 0.025% PVA. Migration current: 125 μA . Sample: 3.5 μl of a mixed solution of 0.8×10^{-3} M. Zones: 1 = Cl^- ; 2 = NO_3^- ; 3 = CrO_4^{2-} ; 4 = SO_4^{2-} ; 5 = MoO_4^{2-} ; 6 = WO_4^{2-} ; 7 = HVO_4^{2-} ; 8 = CO_3^{2-} ; 9 = β -alanine.

Fig. 4 shows an isotachopherogram of the separation of metal oxo anions in the presence of nitrate, chromate and sulphate ions. The analysis time was within 20 min.

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