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Note

Separation of molybdophosphate and molybdosilicate in a non-aqueous system by isotachophoresis

HITOSHI YOSHIDA* and MINEMASA HIDA
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060 (Japan)
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Heteropolymolybdates possess interesting chemical properties for analytical applications. It is well known that they are useful in the spectrophotometric determination of phosphate, silicate and arsenate. However, they sometimes interfere with each other during analysis owing to their similar characteristics, so troublesome procedures are occasionally required.

We have already shown that capillary isotachophoresis (CITP) is useful for the separation of metal ions or metal complexes using complex-forming or ion-pairing equilibria[1–4]. However, there are several problems in CITP with ordinary migrating systems. For example, CITP requires a relatively high concentration of sample and cannot be applied to insoluble substances, such as an ion-asociated complex or a chelate complex formed in aqueous solution, and it is also affected a great deal by the coexisting ions. We have recently demonstrated that the use of a non-aqueous migrating system can overcome these problems in the separation of cationic metal chelates of 1,10-phenanthroline in acetonitrile[3] and of anionic chloro complexes in N,N-dimethylformamide (DMF)[4] after extraction as metal–diethyldithiocarbamate chelates[5].

This paper reports an investigation of the use of CITP with a non-aqueous migrating system in the separation of phosphate as molybdophosphate ion (Mo-P) from a large excess of silicate ion, partially extracted as molybdosilicate ion (Mo-Si).

EXPERIMENTAL

A capillary tube isotachophoretic analyser Model IP-1B with a potential gradient detector (Shimadzu, Kyoto, Japan) was employed. The separation was carried out in a PTFE capillary tube (20 cm × 0.5 mm I.D.). All chemicals used were of the highest grade commercially available. Potasium dihydrogen phosphate, sodium metasilicate and arsenate, and ammonium molybdate were purchased from the Wako, and Capriquat was available from the Dojindo Labs. (Kumamoto, Japan).

Extraction procedure

The extraction procedures were based on investigations by Akaiwa *et al.*[6]. To a test tube, *ca.* 45 ml of twice-distilled water, 4 ml of phosphate solution (10 ppm), adequate amounts of ammonium molybdate (10 w/w%) and hydrochloric acid (ratio

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1:4), and 1 ml of chloroform solution containing 0.01 *M* Capriquat were added. The mixture was shaken vigorously for 1 min and allowed to separate for 5 min. A few microlitres of the organic solution were injected into the CITP system.

RESULTS AND DISCUSSION

Perchloric acid is a stronger acid than hydrochloric acid in dipole aprotic solvents, such as acetonitrile and DMF. These acids were selected as the leading and terminating electrolyte systems (Table I). In this system, ClO_4^-, Cl^- and H^+ serve as leading, terminating and counter ions, respectively.

The effect of the concentration of H^+ as a counter ion on PR values of heteropolymolybdates is shown in Fig. 1. (The PR value is the ratio of the potential gradient of the leading zone to that of the sample zone.) The PR values of the heteropolymolybdate ions decreased as $[H^+]$ increased, because of the effect of ion-pairing equilibria between H^+ and the heteropolymolybdate ions. The differences in the PR values between Mo-Si and Mo-P or Mo-As are large enough for them to be separated, but the PR values of the Mo-P and the Mo-As are nearly equal.

Many workers have studied the effect of various agents on the extraction of heteropolymolybdates[6–9]. In this study, the ion associations of Mo-Si or Mo-P with Capriquat investigated by Akaiwa *et al.* were used to extract molybdophosphate in chloroform. Then the extract was injected into a DMF migrating system. Fig. 2 illustrates the relationship between the PR value or zone length and the concentration of (a) ammonium molybdate or (b) hydrochloric acid in the aqueous solution before extraction. The zone length corresponds to the extraction efficiency. The PR value of Mo-P was almost independent of these reagents, whereas the zone length of Mo-P was drastically affected. It is suggested that the composition of the migrating species does not change but that the extraction efficiency varies considerably in this range of conditions. An increase in the concentration of hydrochloric acid results in a decrease in the zone length of Mo-P, because of ion-pairing equilibria between H^+ and Mo-P. These results agree with the analytical and spectrophotometric data of Akaiwa *et al.* Higher concentrations of ammonium molybdate led not only to an increased zone length of the molybdate ion, which migrated faster than Mo-P, but also to a large amount of Mo-Si in the extract, which formed precipitates in chloroform on standing. Lowering the concentration of hydrochloric acid prevented formation of the heteropolymolybdates.

As a result of this research, phosphate levels of several ppm were speparated from silicate (present in 500-fold times excess) as heteropolymolybdates in the non-

TABLE I

OPERATING SYSTEM

	Leading electrolyte	*Terminating electrolyte*
Solvent	N,N-Dimethylformamide	N,N-Dimethylformamide
Anion	ClO_4^-	Cl^-
Counter ion	H^+	H^+
Concentration	5–20 m*M*	20 m*M*
Current	45–125 μA	

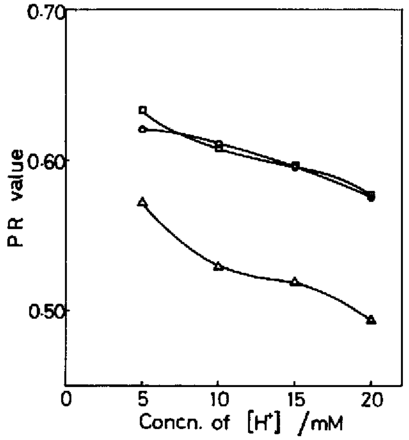
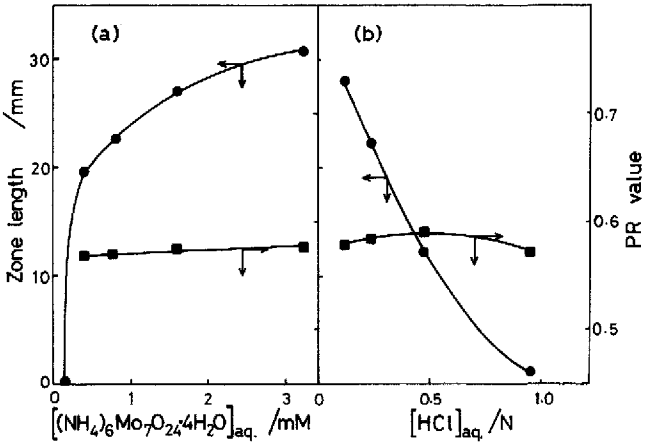


Fig. 1. Effect of the concentration of H^+ on PR values of heteropolymolybdates. Curves: ○ = molybdoarsenate; □ = molybdophosphate; △ = molybdosilicate.

aqueous CITP system after solvent extraction as heteropolymolybdate-Capriquat (Fig. 3). The relative standard deviation of this method for the detrmination of phosphate ion is *ca.* 10% for $1 \cdot 10^{-5}$ *M* in aqueous solution. It is now necessary to develop a suitable procedure for the quantitative analysis.



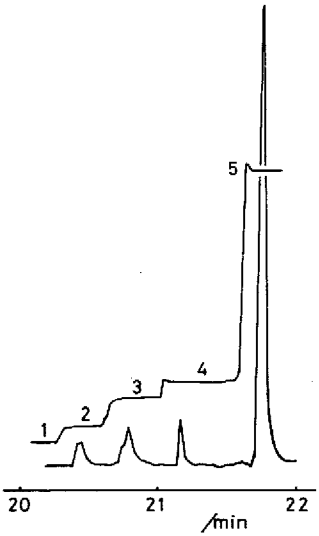


Fig. 2. Effect of the concentration of (a) ammonium molybdate and (b) hydrochloric acid in aqueous solution on the zone length (●) and PR value (■) of Mo-P, with 5 m*M* ClO_4^- and 20 m*M* Cl^- as leading and terminating ion, respectively. Driving current, 45 μA. In (a) the concentration of hydrochloric acid was 0.24 *N*, and in (b) the concentration of ammonium molybdate was 0.31 m*M*.

Fig. 3. Isotachopherogram obtained with 8 m*M* ClO_4^- and 20 m*M* Cl^- as leading and terminating ion, respectively. Driving current, 50 μA; $[PO_4^{3-}] = 1 \cdot 10^{-5}$ *M*, $[SiO_3^{2-}] = 5 \cdot 10^{-3}$ *M* before extraction. Injection volume of organic solution, 5 μl. Peaks: 1 = ClO_4^-; 2 = Mo; 3 = Mo-P; 4 = Mo-Si; 5 = Cl^-.

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