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Note

Capillary tube isotachophoretic separation of heavy metal ions using complex-forming equilibria between cyanide as terminating ion and the metal ions

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Various attempts have been made to improve the separating power of capillary tube isotachophoresis (CITP)[1,2]. The use of complex-forming equilibria is one of the most effective methods for the separation of metal ions, and we have also shown that this method is useful for the separation of alkaline earth metals[3], lanthanides[4], and heavy metals[5]. In most such cases complexing agents were added to the leading electrolyte as a counter-ion or an additive such as a neutral complexing ligand[6,7], and the mobilities of sample ions could be adjusted by the interaction between ligand in the leading electrolyte and the sample ion. On the other hand, the use of complex-forming equilibria between a ligand in the terminating electrolyte and the sample ion has been reported[8,9]. This method was based on using chloride as a terminating ion and the migration of metal ions as metal-chloro complexes with negative charges. In this method, however, a non-aqueous solvent such as dimethylformamide had to be used to suppress the dissociation of hydrogen chloride and make the effective mobility of chloride low enough for it to be used as the terminating ion.

In this study, the isotachophoretic separation of heavy metal ions using the complex-forming equilibria with cyanide as the terminating ion in aqueous solvent was investigated. Cyanide was selected as the terminating ion because it forms complexes strongly with many heavy metal ions in aqueous solvents and its mobility can be adjusted by the pH of the leading electrolyte on basis of the acid–base equilibria. In this operating system, the migrating behaviour of heavy metal ions was studied, and the separation of six metal ions was achieved.

EXPERIMENTAL

Apparatus

A Model IP-1B capillary tube isotachophoretic analyser equipped with a potential gradient detector (Shimadzu, Kyoto, Japan) was used. The PTFE tube for the separation consisted of a main capillary column (150 mm × 0.5 mm I.D.) and a pre-column (40 mm × 1.0 mm I.D.). The current was stabilized at 50–150 μA for 5–15 mM leading electrolyte. The capillary tube was filled with electrolyte by carrier gas (nitrogen).

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TABLE I

OPERATING SYSTEM

Parameter	*Leading electrolyte*	*Terminating electrolyte*
Anion	Cl^- or NO_3^-	CN^-
Counter-ion	$TrisH^+$	K^+
Concentration	5–15 m*M*	10 m*M*
Additive	0.005% Poly(vinyl alcohol)	5 m*M* Barium hydroxide

Reagents

Hydrochloric acid and poly(vinyl alcohol) were of analytical-reagent grade and were used without further purification.

Stock standard solutions of metal ion such as mercury(II), cadmium(II), silver(I), zinc(II), cobalt(II) and copper(II) were prepared by dissolving their chlorides or nitrates in water.

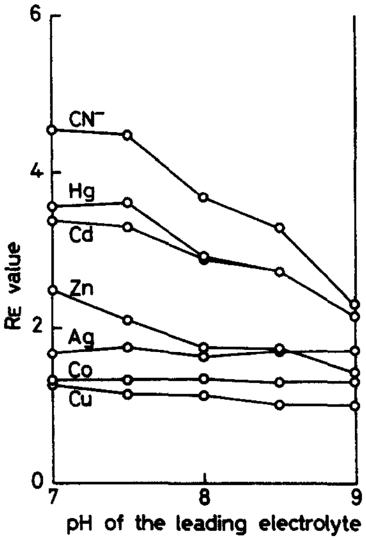
The leading electrolyte was prepared by diluting a stock solution of 2 *M* hydrochloric acid and 1% poly(vinyl alcohol), and the pH was adjusted by adding tris(hydroxymethyl)aminomethane. The terminating electrolyte was prepared by diluting a stock solution of 1 *M* potassium cyanide. Barium hydroxide (5 m*M*) was added to the terminating electrolyte to exclude carbonate ion. The operating system is shown in Table I.

RESULT AND DISCUSSION

In isotachophoretic migration, it is necessary that the difference between the effective mobilities of the leading and terminating ions is sufficiently great. When chloride is used as the terminating ion, a non-aqueous solvent had to be used as the migrating system to suppress the dissociation of hydrogen chloride and lower its mobility[8,9]. Since the cyanide ion is strongly alkaline (its dissociation constant pK_a is 9.4), its effective mobility can be controlled by the pH of leading electrolyte in aqueous solution. At pH *ca.* 7–9 of the leading electrolyte, this mobility is low enough for cyanide to be used as the terminating ion, and there is a sufficient difference in potential gradient between the leading ion and the terminating ion.

When heavy metal ions are injected into this system, they migrate to the terminating side (cathode) because of their positive charge, where they react with cyanide ion to form cyano-complexes with a negative charge, and thence migrate to the leading side (anode). The zones of metal ions could be detected between leading and terminating ions in isotachopherograms.

The effect of the pH of the leading electrolyte on the effective mobilities of cyano-complexes is shown in Fig. 1. The R_E value in the diagram represents the ratio of the potential gradient of sample ions or terminating ion to that of leading ion. The R_E values of most of the cyano-complexes and the cyanide ion decrease with increasing pH. An increase in the pH of the leading electrolyte promotes the dissociation of hydrogen cyanide and increases the concentration of cyanide available for complex formation. Therefore, the conditional stability constants of the cyano-complexes increases with increasing pH, and complexes with a greater negative charge and higher mobility could be formed.



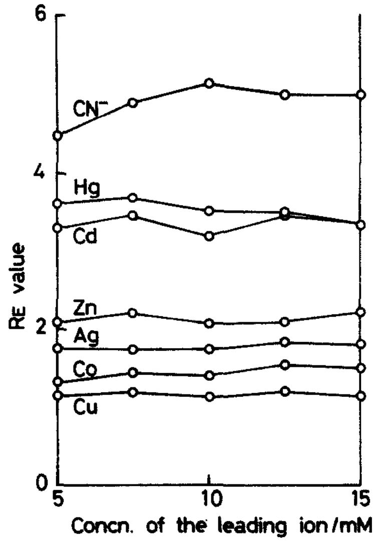


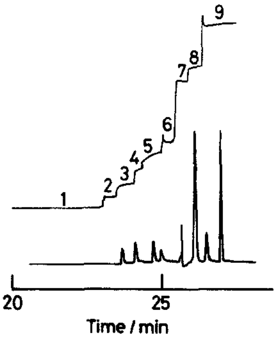
Fig. 1. Effect of the pH of the leading electrolyte on the R_E values of cyano-complexes. The concentration of the leading ion (Cl^-) was constant at 5 m*M*. Driving current, 50 μA.

Fig. 2. Effect of the concentration of the leading ion on the R_E values of cyano-complexes. The pH was constant at 7.5. Driving current, 50–150 μA.

The effective mobilities of cobalt(II) and copper(II) cyano-complexes below pH 7.0 and of mercury(II) and cadmium(II) above pH 8.0 are similar, and those ions cannot be separated. Also, above pH 8.5, the mobility of copper(II) is similar to that of the leading ion, and the copper(II) cyano-complex cannot be detected. The cyano-complexes of six metal ions can be separated at pH 7.5.

The cyano-complex of copper(II) is reduced to copper(I), and it seems that this reaction occurred in this system.

In isotachophoresis, the concentration of each zone is adjusted with the concentration of leading electrolyte[10]. The concentration of cyanide ion that is supplied from terminating zone and acts as a complex agent may be also affected by the concentration of the leading electrolyte. Therefore, the effect of the concentration of the leading electrolyte on the effective mobilities of cyano-complexes was investigated (Fig. 2). Most of the effective mobilities were constant at concentrations of the leading electrolyte in the range 5–15 m*M*, although those of the mercury(II) and cadmium(II) cyano-complexes decreased slightly with increasing concentration of the leading electrolyte. This can be explained as follows. The effective mobility of cyano-complexes depends on the fractions of the various polyligand complexes, and the larger the fraction of polyanionic species, the higher the effective mobility. Therefore the differenc of effective mobilities of cyano-complexes become large with increasing the difference between the fractions of anionic complexes of each metal ion. The results calculated using stability constants[11] showed that the difference of fraction for cyano-complexes of mercury and cadmium, which are bivalent anionic species, becomes smaller as the concentration of cyanide increases. This is identical with experimental results, *i.e.* the mobility of each metal complex depends on its stability constant. In



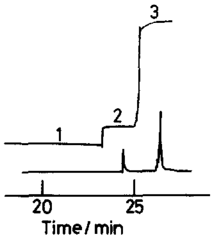


Fig. 3. Isotachopherogram of cyano-complexes: 1 = Cl^-; 2 = copper; 3 = cobalt; 4 = silver; 5 = carbonate; 6 = zinc; 7 = cadmium; 8 = mercury; 9 = CN^-. Leading electrolyte, 5 m*M* hydrochloric acid–Tris, 0.005% poly(vinyl alcohol) (pH 7.5). Sample size, 10 μl of a mixed solution of 0.5 m*M*. Driving current, 50 μA.

Fig. 4. Isotachopherogram of ferricyanate: 1 = NO_3^-; 2 = ferricyanate; 3 = CN^-. Leading electrolyte; 5 m*M* nitric acid–Tris, 0.5 m*M* lanthanum nitrate, 0.005% poly(vinyl alcohol) (pH 7.5). Sample size, 5 μl of 1 m*M* potassium ferricyanate. Driving current, 50 μA.

particular, the consecutive stability constants concerned with the formation of anionic species play an important rule in the separation. The optimum pH for the leading electrolyte, 5 m*M* hydrochloric acid–Tris, is 7.5.

In this system, six metal ions could be separated as shown in Fig. 3. The order of their effective mobilities is mercury < cadmium < zinc < silver < cobalt < copper, which follows the order of the stability constants of their cyano-complexes (except mercury). The zone of carbonate ion was detected between the zones of silver(I) and zinc(II). Carbonate ion could not be excluded completely by addition of barium hydroxide to the terminating electrolyte. Calibration curves for each metal ion were linear in the range 4–20 nmol injected, in 20 μl of sample.

The zones of iron(II), iron(III), and nickel(II) cyano-complexes could not be detected in this system. The effective mobilities of iron(II) and iron(III) cyano-complexes would be larger than that of the leading ion, because their stability constants are sufficiently large to form cyano-complexes with more negative charge than that of other metals ions. The use of ion-pairing equilibria with lanthanum(III) added to the leading electrolyte enabled the zone of the ferricyano-complex to be detected (Fig. 4).

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