

CHROM. 21426

Note

Isotachophoretic separation of cyano complexes of noble metals using ion-pairing equilibrium in water–acetonitrile solvent

SHUNITZ TANAKA, TAKASHI KANETA and HITOSHI YOSHIDA*

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060 (Japan)

(First received November 8th, 1988; revised manuscript received February 3rd, 1989)

Noble metals in the form of cyano complexes are widely used for metal plating in industry and for ornaments and many methods for their determination have been reported, *e.g.*, spectrophotometry¹, chromatography^{2–4}, atomic absorption spectrometry⁵ and inductively coupled plasma atomic emission spectrometry⁶.

Recently, we reported an isotachophoretic method for the determination of heavy metal ions as cyano complexes⁷. In this method, the metal cations injected were converted into cyano complexes by reaction with cyanide in the terminating electrolyte in the migration column and migrated as negatively charged ions. The effective mobility of each cyano complex was controlled by complex-forming equilibria between the metal ions and the cyanide in the terminating electrolyte and by the pH of the leading electrolyte. However, application of this migration system to the separation of noble metal ions was difficult because most noble metal ions form very stable or inert complexes with cyanide, which makes it impossible to control the mobilities of such complexes only by complex-forming equilibria with the terminating ion. It is known to be effective to use the interaction of a counter ion or additive in the leading electrolyte in order to control the mobility^{8,9}. Therefore, in this work, we attempted to use ion-pairing equilibria to separate the cyano complexes of noble metal ions, such as palladium, platinum, gold, silver and nickel. It was established that using ion-pairing equilibria between these complex anions and a bivalent complex counter cation in water–acetonitrile is effective in achieving the required separation.

EXPERIMENTAL

Apparatus

A Model IP-1B capillary tube isotachophoretic analyser (Shimadzu, Kyoto, Japan), equipped with a potential gradient detector and a column system consisting of a PTFE pre-separation capillary (50 × 1.0 mm I.D.) and a PTFE analytical capillary column (150 × 0.5 mm I.D.), was used. The current was stabilized at 50 μ A after migration at 100 μ A for 8–10 min. The capillary tube was filled with the leading and the terminating electrolytes by pressure of nitrogen gas.

Reagents

Hydrochloric acid, tris(hydroxymethyl)aminomethane (Tris), tetradecyldimethylbenzylammonium chloride (Zephiramine) and poly(vinyl alcohol) were of analytical-reagent grade from Wako (Osaka, Japan) and were used without further purification.

Stock solutions of cyano complexes of nickel(II), platinum(II), silver(I) and gold(I) were prepared by dissolving potassium tetracyanonickolate(II), barium tetracyanoplatinate(II), potassium dicyanoargenate(I) and potassium dicyanoaurate(I) (Wako) in water. Potassium tetracyanopalladate(II) and tris(1,10-phenanthroline)-iron(II) chloride were synthesized as described below¹⁰.

Synthesis of potassium tetracyanopalladate(II). Palladium chloride (1 g) was dissolved in 70 ml of 0.01 M hydrochloric acid and 1 M potassium cyanide solution was added to it until palladium cyanide precipitated. The precipitate was filtered off and dissolved in potassium cyanide solution. After evaporation, the residual solid was recrystallized from water.

Synthesis of tris(1,10-phenanthroline)iron(II) chloride. Iron(II) chloride and 1,10-phenanthroline in a molar ratio of 1:3 were dissolved in methanol and the solution was filtered. Acetone was added and the required compound precipitated. The precipitate was recrystallized from water.

Electrolytes

The operational electrolyte system is shown in Table I. Tris-HCl buffer, the molar ratio of which was constant at 2.5:1, was used as the leading electrolyte at a pH of ca. 8.4. The concentration of the leading ion was constant at 6 mM. A mixture of acetonitrile and water was used as the solvent to prevent the precipitation of ion pairs and to adjust the ion-pairing equilibria.

RESULTS AND DISCUSSION

In a previous paper⁷, we reported that six heavy metal ions could be separated by isotachophoresis by using complex-forming equilibria with cyanide as the terminating ion. However, cyano complexes of noble metal ions which have high stability constants could not be detected because of their mixing with the leading zone owing to their high mobilities. These complexes would be detectable by adding an ion-pairing reagent to leading electrolyte. When tris(1,10-phenanthroline)iron(II) or Ze-

TABLE I
OPERATING SYSTEM

	Leading electrolyte	Terminating electrolyte
Anion	6 mM Cl ⁻	10 mM CN ⁻
Counter ion	TrisH ⁺ ^a	K ⁺
Co-counter ion	Zephiramine, Fe(phen) ₃ ²⁺	
Additive	0.01% poly(vinyl alcohol)	50 mM Ba(OH) ₂
Solvent	Water-acetonitrile	Water

^a Tris:HCl = 2.5:1.

phiramine was used as the ion-pairing reagent, the effective mobilities of these cyano complexes decreased owing to the ion-pairing equilibria and the zone could be detected. Then the use of a mixed solvent (water-acetonitrile) was necessary to prevent precipitation of the ion-pair.

The influence of the concentration of the ion-pairing reagents on the R_E values (ratio of the potential gradient of the sample zone to that of the leading zone) of the cyano complexes is shown in Figs. 1 and 2. The effective mobilities of the cyano complexes decreased as the concentration of Zephiramine and tris(1,10-phenanthroline)iron(II) increased and the differences in the mobilities of the cyano complexes increased. With 1 mM tris(1,10-phenanthroline)iron(II) the differences in the mobilities of the complexes were greater than those using zephiramine.

The presence of acetonitrile influences the effective mobilities of the cyano complexes. The effect of acetonitrile on the effective mobilities with 1 mM tris(1,10-phenanthroline)iron(II) is shown in Fig. 3. At 0–5% (v/v) of acetonitrile, nickel and platinum or silver and gold could not be separated. When the concentration of acetonitrile was greater than 10%, the difference in mobilities increased and separation could be achieved. This effect of acetonitrile is related to the formation of ion pairs. The interaction of an ion pair is generally stronger in aqueous than in organic solutions. The interaction of the cyano complexes and the ion-pair reagent in aqueous solution is too strong to cause sufficient differences in the mobilities of the cyano complexes. However, by adding acetonitrile, this interaction becomes weaker so that each cyano complex can be separated. This was confirmed by the fact that the conductivity of the ion pair was greater in 20% acetonitrile solution than in aqueous solution using the ion pair of tris(1,10-phenanthroline)iron(II) and dicyanoargentate.

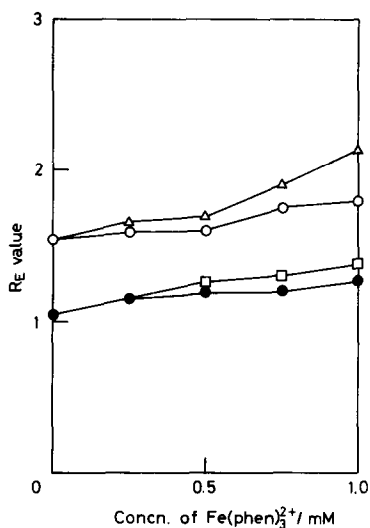
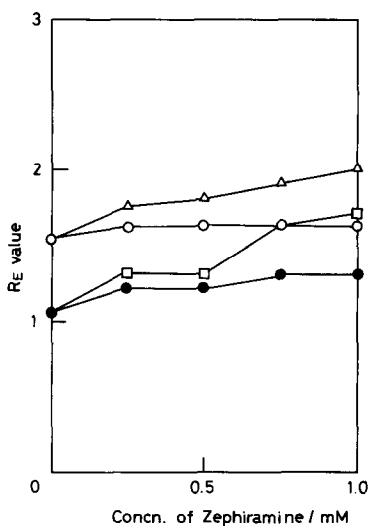


Fig. 1. Effect of concentration of zephiramine in leading electrolyte on R_E values of cyano complexes. Concentration of acetonitrile, 20% (v/v). ● = Nickel; □ = platinum; ○ = silver; △ = gold.

Fig. 2. Effect of concentration of tris(1,10-phenanthroline)iron(II) in leading electrolyte on R_E values of cyano complexes. Concentration of acetonitrile, 20% (v/v). Symbols as in Fig. 1. phen = 1,10-Phenanthroline.

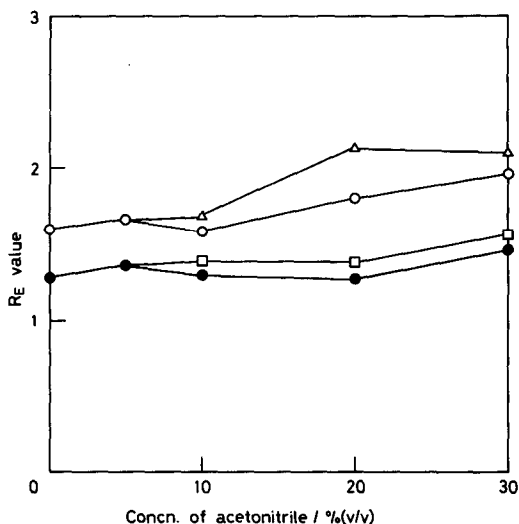


Fig. 3. Effect of concentration of acetonitrile in leading electrolyte on R_E values of cyano complexes. Concentration of tris(1,10-phenanthroline)iron(II), constant at 1 mM. Symbols as in Fig. 1.

An isotachopherogram of four cyano complexes with 20% acetonitrile solution containing 1 mM tris(1,10-phenanthroline)iron(II) is shown in Fig. 4. The order of their mobilities was nickel > platinum = palladium > silver > gold. Although nickel and platinum, or silver and gold, had very close mobilities in a migration system without an ion-pair reagent, the difference between the mobilities of the complexes increased as a result of ion-pairing equilibria and they could be separated. However, the cyano complexes of palladium and platinum showed the same isotachopheretic behaviour and they could not be separated even utilizing ion-pairing equilibria.

Under these conditions the calibration graphs of each metal ion were linear in the range 1–5 nmol. The reproducibilities of the zone length at 1 and 5 nmol are given

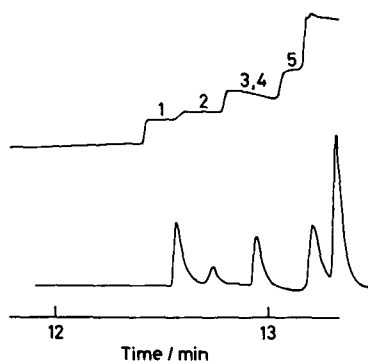


Fig. 4. Isotachopherogram of cyano complexes. Leading electrolyte, 20% (v/v) acetonitrile solution containing 1 mM tris(1,10-phenanthroline)iron(II). 1 = Nickel; 2 = platinum; 3 = hydrogencarbonate; 4 = silver; 5 = gold.

TABLE II
PRECISION OF ZONE LENGTH

Metal ion	Amount (nmol)	Zone length (s)	R.S.D. ^a (%)	Number of determinations
Nickel	1	5.2	5.9	4
	5	24.0	2.6	5
Platinum	1	5.1	1.1	4
	5	21.6	1.5	5
Silver	1	13.3	0.4	4
	5	26.1	0.6	5
Gold	1	3.6	4.2	4
	5	17.1	2.1	5

^a Relative standard deviation.

in Table II. Except for 1 nmol of nickel, the reproducibilities were below 5%. The zone of silver became longer because of the formation of a mixed zone with hydrogencarbonate. The zone of hydrogencarbonate did not disappear completely on addition of 10 mM barium chloride to the sample solutions. A migration system of low pH is necessary to separate the silver zone from the hydrogencarbonate zone. However, when 10 mM barium chloride was added to all samples, the calibration graph of silver was linear and the slope was the same as that of monovalent dicyanoaurate. Therefore, from the linearity of the calibration graph, the zone length of hydrogencarbonate could be calculated.

This migration system could be applied not only to cyano complexes but also to metal chloride solutions as sample. Noble metal ions injected were converted into cyano complexes by reaction with cyanide as the terminating ion and could migrate as the anion. With the present method, it was found that the use of ion-pairing equilibria was effective for the separation of cyano complexes of noble metal ions.

REFERENCES

- 1 F. E. Beamish, *The Analytical Chemistry of the Noble Metals*, Pergamon Press, Oxford, 1966.
- 2 D. F. Hilton and P. R. Haddad, *J. Chromatogr.*, 361 (1986) 141.
- 3 B. Grigorova, S. A. Wright and M. Josephson, *J. Chromatogr.*, 410 (1987) 419.
- 4 P. R. Haddad and N. E. Rochester, *Anal. Chem.*, 60 (1988) 536.
- 5 T. Groenewald, *Anal. Chem.*, 40 (1968) 863.
- 6 R. B. Wemyss and R. H. Scott, *Anal. Chem.*, 50 (1978) 1694.
- 7 S. Tanaka, T. Kaneta and H. Yoshida, *J. Chromatogr.*, 447 (1988) 383.
- 8 P. Boček, I. Miedziak, M. Deml and J. Janák, *J. Chromatogr.*, 137 (1977) 83.
- 9 I. Nukatsuka, M. Taga and H. Yoshida, *J. Chromatogr.*, 205 (1981) 95.
- 10 T. Tachibana (Editor), *Shin-jikken-kagaku-kohza*, Vol. 8(II), Maruzen, Tokyo, 1977.