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SEPARATION OF CATIONIC METAL CHELATES OF 1,10-PHENANTHROLINE BY CAPILLARY TUBE ISOTACHOPHORESIS IN NON-AQUEOUS SYSTEMS

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SUMMARY

The separation and migration behaviour of cationic 1,10-phenanthroline (phen)chelates of Ni(II), Fe(II), Co(II), Cu(II), etc., have been investigated by capillary tube isotachophoresis (CITP) using acetonitrile as electrolyte. The effective mobilities of the Co(II)– and Cu(II)–phen chelates decreased with decreasing radius of the counter ion (perchlorate > iodide > bromide > chloride). The chelates of Fe(II), Co(II) and Cu(II) or Ni(II), Co(II) and Cu(II) were separated when chloride was used as counter ion. It is suggested that the ligand-replacement and/or dissociation equilibria between the metal chelates and counter anion or ligand species play an important rôle in controlling the effective mobilities of the metal chelates, and that the Cu(II)–phen chelate may migrate as a five-coordinated complex, $[Cu(phen)_2Cl]^+$, in this system. The combination of CITP and solvent extraction was also tried for metal ions in concentrations of the order of 10^{-5}–10^{-6} M in aqueous solution.

INTRODUCTION

Many methods have been developed to improve the separability of capillary tube isotachophoresis (CITP). The ion-pairing or complex-forming equilibria between sample species and the counter ion of the leading electrolyte have frequently been used to control the effective mobilities of sample species[1–4]. However, these studies were usually undertaken in aqueous solutions. If the same effects could be utilized in non-aqueous solvents the potential of CITP would be extended to the separation of species that are either insoluble or only slightly soluble in water but extractable in organic solvents as charged species[5].

The use of non-aqueous solvents also makes possible the separation and determination of trace species in aqueous solution by combined use of solvent extraction and CITP. One of the types of species extractable into organic solvents is the ion-pair ternary complex such as $M(phen)_3(ClO_4)_2$[6]. These 1,10-phenanthroline (phen) chelates dissociate to some extent into charged species in nitrobenzene. Therefore, it should be possible to separate such metal chelates by CITP using an appropriate organic solvent as the electrolyte solution.

O'Laughlin and Hanson[7,8] have recently reported the separation of the metal complexes $Fe(phen)_3^{2+}$, $Ni(phen)_3^{2+}$ and $Ru(phen)_3^{2+}$ by use of ion-pair high-performance liquid chromatography. Lederer and co-workers[9-11] found by paper electrophoresis that the effective mobilities of metal chelates such as $Co(phen)_3^{3+}$, $Co(en)_3^{3+}$ (en = ethylenediamine), $Co(NH_3)_6^{3+}$, etc., are considerably influenced by the surrounding anions owing to ion-pair formation. However, no attempt was made by CITP to separate those metal complexes in a non-aqueous solvent.

The purpose of this paper is to demonstrate the analytical potential of CITP for metal chelates such as the 1,10-phenanthroline chelates of Ni(II), Fe(II), Co(II) and Cu(II). We also wished to confirm that in non-aqueous solvents the interactions such as ion association, complex formation and/or ligand-replacement equilibria between the metal chelate and counter ions play an important rôle in controlling the effective mobilities of the chelate species in CITP. The combined use of solvent extraction and CITP was also tried for trace metal ions in aqueous solutions.

EXPERIMENTAL

Apparatus

A capillary tube isotachopheretic analyzer Model IP-1B with potential gradient detector (Shimadzu, Kyoto, Japan) was employed. The separations were carried out in a PTFE capillary tube (30 cm × 0.5 mm I.D.). A stabilized current of 125 μA was used as a driving current.

A digital conductometer Model CM-15 (TOA Electronics Ltd.) was used for measuring the conductance.

Reagents

Stock solutions of metal chelates of 1,10-phenanthroline were prepared by dissolving metal(II) salts and slightly more than 3 mol equiv. of 1,10-phenanthroline monohydrate in methanol and diluting to 0.01 M metal(II) ion in methanol. The metal(II) salts were acetates, except for ion(II) chloride. Tetraethylammonium chloride, bromide, iodide and perchlorate and 1,10-phenanthroline monohydrate were from Wako Pure Chemical Ind. Acetonitrile and other chemicals were analytical reagent grade and used without further purification.

RESULTS AND DISCUSSION

Operating system

After preliminary experiments it was found that some metal chelates of 1,10-phenanthroline could easily be detected when acetonitrile was used as the electrolyte solution. The operating system in Table I was chosen. The advantage of acetonitrile as electrolyte in CITP is that it has a comparative high boiling point and high dielectric constant, and is easily miscible with both water and other organic solvents.

In order to study the effect of the counter ion, tetraethylammonium chloride, bromide, iodide or perchlorate was used as the leading electrolyte. 1,10-Phenanthroline monohydrate was added to suppress the dissociation of the 1,10-phenanthroline chelates. 1,10-Phenanthroline hydrochloride was used as the terminating electrolyte. Its protonated ion phenH$^+$ acts as the terminating ion.

TABLE I

CITP OPERATING SYSTEM

	Leading electrolyte	Terminating electrolyte
Solvent	Acetonitrile	Acetonitrile
Cation	Tetraethylammonium (TEA$^+$)	phenH$^+$
Counter ion (5 mM)	Cl$^-$, Br$^-$, I$^-$, ClO$_4^-$	Cl$^-$
Additive (3 mM)	1,10-Phenanthroline	

Effect of counter ion. Fig. 1 shows the effects of counter anions on the effective mobilities of the phen chelates. Their PR values are plotted against the radius of the counter ion in the leading electrolyte. The PR value in CITP represents the ratio of the potential gradient of the leading zone to that of the sample zone, and is equal to the ratio of the effective mobility of the sample ion to that of the leading ion. In spite of a change of counter ion, the PR values for the Ni(II)– and Fe(II)–phen chelates were almost constant, but those for the Co(II)– and Cu(II)–phen chelates and phenH$^+$ decreased in order of decreasing radius of the counter ion (perchlorate > iodide > bromide > chloride). The PR values of the Zn(II)–, Cd(II)– and Mn(II)– phen chelates were approximately equal to those of the Ni(II)–, Fe(II)– or Co(II)– phen chelate when perchlorate was used as counter ion, but the zones of the former chelates could not be observed when chloride was used as counter ion.

Fig. 2 shows the isotachopherograms of three phen chelates of Fe(II), Co(II) and Cu(II) under the conditions in Table I. When perchlorate or iodide was used as counter ion in the leading electrolyte, the three metal chelates were detected as a mixed zone, and the results were not always consistent with those expected from Fig. 1. However, the use of bromide ion made it possible to separate the Cu(II)–phen
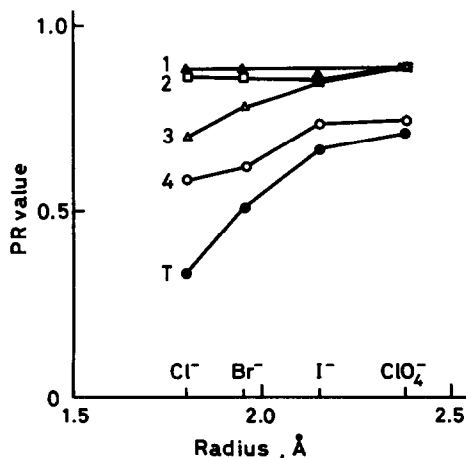

Fig. 1. PR values of some 1,10-phenanthroline metal chelates for different complex-forming anions. The operating conditions are summarized in Table I. Curves: 1 = Ni(II)–; 2 = Fe(II)–; 3 = Co(II)–; 4 = Cu(II)–phen chelate; T = terminating ion.
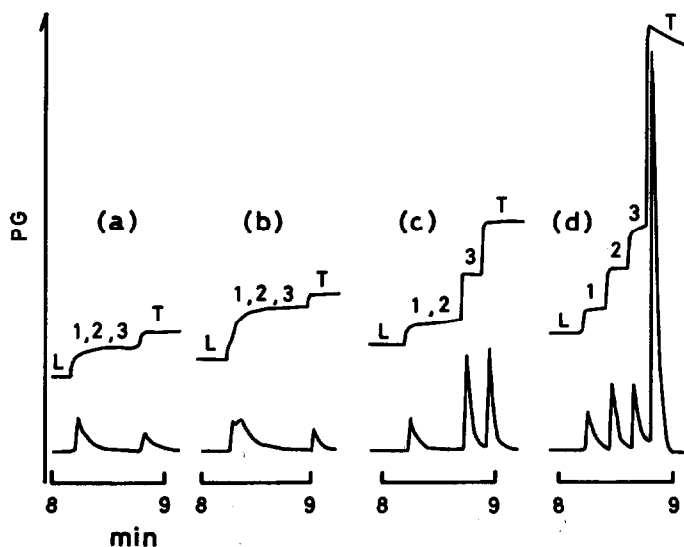
Fig. 2. Isotachopherograms of the phen chelates of Fe(II), Co(II) and Cu(II). The counter ion of the leading electrolyte was ClO_4^- (a), I^- (b), Br^- (c) and Cl^- (d). Conditions as in Fig. 1. 1 = Fe(II)-; 2 = Co(II)-; 3 = Cu(II)-phen chelate; L = leading ion; T = terminating ion. Amount of each metal chelate was 4 nmole. PG = potential gradient.

chelate from the others, and the complete separation of the three metal chelates was achieved when chloride was used as counter ion in the leading electrolyte.

The relationship between the concentration of chloride added as counter ion and the PR values of the metal chelates was investigated keeping constant (5 mM) the concentration of the leading ion (tetraethylammonium) and changing continuously the molar ratio of the counter anion, $[Cl^-]/[ClO_4^-]$. As shown in Fig. 3, the PR values of the Co(II)- and Cu(II)–phen chelates were greatly influenced by chloride ion even when its concentration was low, but were nearly constant at a chloride concentrations more than 25%.
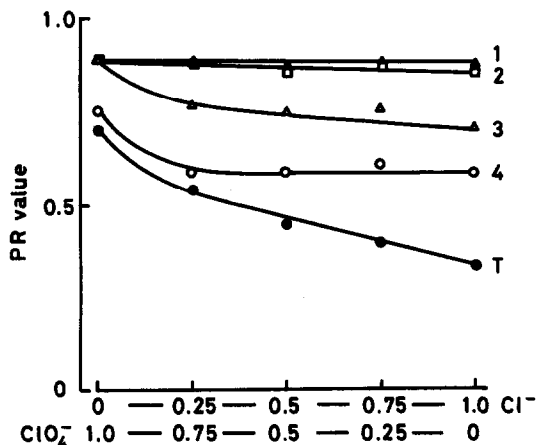

Fig. 3. Effect of the concentration of Cl^- in the leading electrolyte on the PR values of the metal-phen chelates. $[Cl^-] + [ClO_4^-] = 5$ mM. Curves as in Fig. 1.

Effect of 1,10-phenanthroline concentration in the leading electrolyte. Fig. 4 shows the effect of the concentration of 1,10-phenanthroline in the leading electrolyte. The PR values of the Ni(II)- and Fe(II)–phen chelates were almost constant, but that of the Fe(II)–phen chelate was slightly lower than of the Ni(II)–phen chelate when 1,10-phenanthroline was not added. The PR values of the Co(II)–phen chelate increased greatly with increasing 1,10-phenanthroline concentration up to about 4 mM. The PR value of the Cu(II)–phen chelate was low and little affected by the addition of 1,10-phenanthroline.
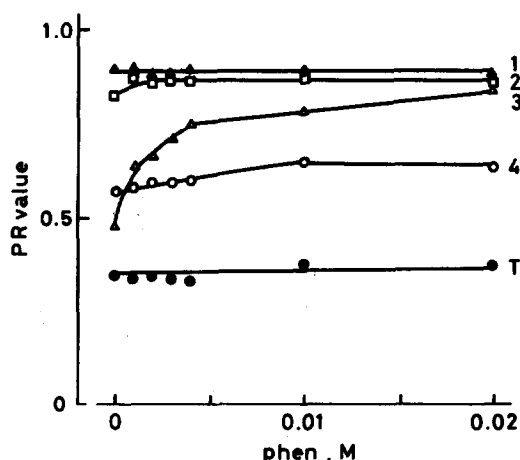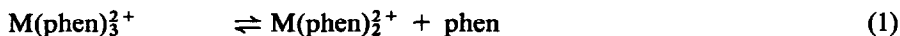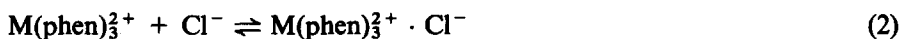

Fig. 4. Effect of the concentration of 1,10-phenanthroline in the leading electrolyte on the PR values of the metal–phen chelates. Chloride was used as the counter ion. Curves as in Fig. 1.

These results suggest that the effective mobilities of the metal–phen chelates are mainly governed by the ligand-replacement equilibria and/or dissociation equilibria between the metal–phen chelates and the counter anion rather than by ion-association complex-forming equilibria. Since the Ni(II)– and Fe(II)–phen chelates are inert inner-orbital complexes and have large stability constants, their PR values may be little influenced by the counter anion. On the other hand, since the Co(II)– and Cu(II)–phen chelates are labile outer-orbital complexes their stability constants are smaller, their effective mobilities may be decreased by ligand-replacement equilibria or ion-association complex-forming equilibria between the metal–phen chelates and the counter anion as follows:
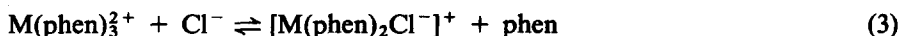
dissociation equilibria

$$M(phen)_3^{2+} \rightleftharpoons M(phen)_2^{2+} + phen \tag{1}$$

ion-association complex-forming equilibria

$$M(phen)_3^{2+} + Cl^- \rightleftharpoons M(phen)_3^{2+} \cdot Cl^- \tag{2}$$

ligand-replacement equilibria

$$M(phen)_3^{2+} + Cl^- \rightleftharpoons [M(phen)_2 Cl^-]^+ + phen \tag{3}$$

Particularly in the case of the Cu(II)–phen chelate, the equilibrium

$$Cu(phen)_3^{2+} + Cl^- \rightleftharpoons [Cu(phen)_2Cl]^+ + phen \tag{4}$$
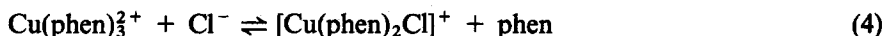
might be shifted significantly to the right even when the chloride concentration is extremely low.

By virtue of these effects, the separability of CITP for these metal chelates might be enhanced.

Simultaneous determination of metal chelates

When the leading electrolyte contains 5 mM tetraethylammonium salt (counter ion concentration ratio, $[Cl^-]/[ClO_4^-]$ = 3) and 3 mM 1,10-phenanthroline, the separation and determination of the phen chelates of Fe(II), Co(II) and Cu(II) or Ni(II), Co(II) and Cu(II) could be achieved with satisfactory results. The calibration curves for the Ni(II)–, Fe(II)–, Co(II)– and Cu(II)–phen chelates were all linear in the range of 1–8 nmol; the slopes for the first three were almost equal, but that of the Cu(II)–phen chelate was about half of these. When 1,10-phenanthroline was not added to the leading electrolyte, the separation of the metal chelates Ni(II)–, Fe(II)–, Co(II)– and Cu(II)–phen was possible as shown in Fig. 5. But under these conditions the reproducibility of the PR values was poor and the order of the PR values for the Co(II)– and Cu(II)–phen chelates was reversed compared with that when the leading electrolyte contained 1,10-phenanthroline.
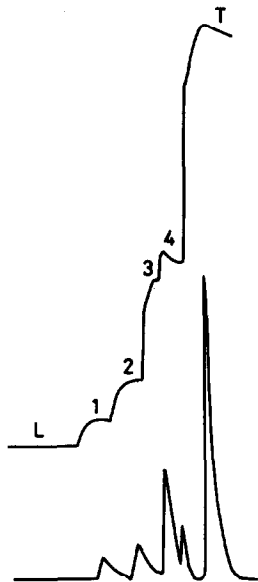

Fig. 5. Isotachopherogram of the phen chelates of Ni(II) (1), Fe(II) (2), Cu(II) (3) and Co(II) (4) when 1,10-phenanthroline was not added in the leading electrolyte. Chloride was used as the counter ion in the leading electrolyte. L = Leading ion; T = terminating ion.

Combined use of solvent extraction and CITP

For the determination of trace levels of metal ions by CITP, a large volume of sample solution must be injected to satisfy the detection limit. But this is undesirable in CITP, so the combined method of solvent extsaction and CITP was studied for such cases. In this method a small amount of nitrobenzene was used to achieve a considerable concentration effect and the extract was directly injected into CITP.

The procedure is as follows. To a separating funnel, about 90 ml of sample solution containing $(2–40) \cdot 10^{-7}$ mol of Fe^{2+}, Co^{2+} and Cu^{2+}, 5 ml of 2 M acetate buffer of pH 6, 1 ml of 0.02 M $KClO_4$ solution and 1 ml of 0.05 M 1,10-phenanthroline solution are added, the contents are diluted to 100 ml in distilled water and extracted with 1–5 ml of nitrobenzene. Ten microlitres of this extract are directly injected into CITP without further treatment.

Table II shows the analytical results obtained by comparison with calibration curves which were made by injecting solutions of the standard metal chelate in methanol without extraction. The error for the mixed sample of concentration 10^{-5}–10^{-6} M was about 20%. Further work may make this method more useful for the separation and determination of trace metal ions in aqueous solution.

TABLE II

COMBINED USE OF SOLVENT EXTRACTION AND CITP

Volume of nitrobenzene used for extraction; A, 1 ml; B, 5 ml.

Concentration in aqueous phase (M)	Recovery (%)					
	Mixed sample			Single sample		
	Fe(II)	Co(II)	Cu(II)	Fe(II)	Co(II)	Cu(II)
A						
$2.0 \cdot 10^{-6}$	98	124	130	102	111	107
$4.0 \cdot 10^{-6}$	98	117	128	105	114	121
$6.0 \cdot 10^{-6}$	98	126	117	110	115	111
$8.0 \cdot 10^{-6}$	94	122	118	102	108	113
B						
$1.0 \cdot 10^{-5}$	89	113	113	98	106	93
$2.0 \cdot 10^{-5}$	82	106	117	95	99	102
$3.0 \cdot 10^{-5}$	91	102	101	100	99	96
$4.0 \cdot 10^{-5}$	81	102	106	93	100	98

Conductometric titration

The electrophoretic behaviour of the Cu(II)–phen chelate was significantly different from that of the Ni(II)–, Fe(II)– or Co(II)–phen chelate. This chelate had a lower PR value than that of other metal–phen chelates even when perchlorate, which has little or no effect even on the Zn(II)–, Cd(II)– and Mn(II)–phen chelates, was used as the counter ion. When chloride was used as the counter ion, the zone length of the Cu(II)–phen chelate was about half of that of the others at the same concentration. This suggests that the charge on the Cu(II)–phen chelate is one. To clarify this, a conductometric study was carried out as follows.

A 50-ml acetonitrile solution containing $5 \cdot 10^{-5}$ mol of copper(II) chloride was titrated conductometrically with 0.02 M 1,10-phenanthroline in acetonitrile solution. Cobalt(II) and zinc(II) chlorides were also titrated for comparison. Fig. 6 shows typical conductometric titration curves for the metal chlorides. Up to a 1:1 molar ratio of phen to Cu(II), a yellowish green precipitate was formed in the acetonitrile solution which dissolved completely before the molar ratio had reached 2:1 (Fig. 6, curve 1). The composition of the precipitate was shown to be Cu(II):phen:Cl = 1:1:2 by means of elemental analysis.
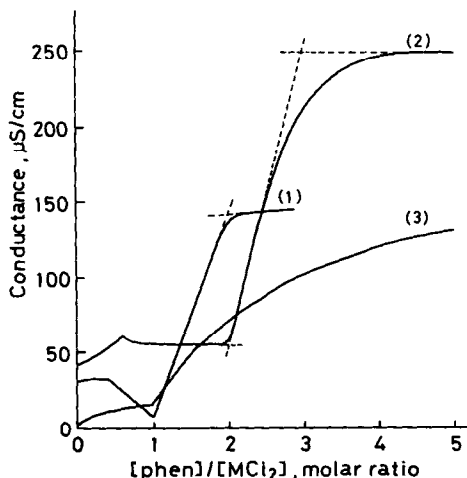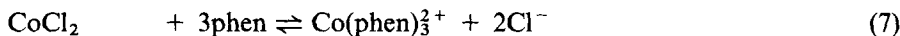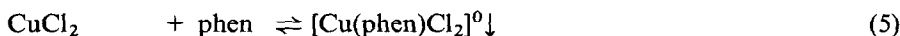

Fig. 6. Typical conductometric titration curves for metal chlorides. Acetonitrile was used as solvent, 0.02 M 1,10-phenanthroline in acetonitrile solution as titrant. Curves: 1 = copper chloride; 2 = cobalt chloride; 3 = zinc chloride.

For cobalt(II) chloride the titration curve showed two inflection points, at molar ratios of phen to Co(II) of 2:1 and 3:1 (Fig. 6, curve 2). On the other hand, the curve for zinc(II) chloride did not have a clear inflection point owing to the low stability constant of the Zn(II)–phen chelate (Fig. 6, curve 3). As shown in Fig. 6, when an excess of 1,10-phenanthroline was added, the conductance of the copper(II) solution was nearly equal to half that of the cobalt(II) solution.

These results suggest that the reactions of 1,10-phenanthroline with metal chloride are as follows:

$$CuCl_2 \quad\quad + \text{ phen} \;\rightleftharpoons\; [Cu(phen)Cl_2]^0 \downarrow \tag{5}$$

$$Cu(phen)Cl_2 + \text{ phen} \;\rightleftharpoons\; [Cu(phen)_2Cl]^+ + Cl^- \tag{6}$$

$$CoCl_2 \quad\quad + \text{ 3phen} \rightleftharpoons Co(phen)_3^{2+} + 2Cl^- \tag{7}$$

The existence of the five-coordinated Cu(II)–phen chelate, $[Cu(phen)_2Cl]^+$, in nitrobenzene is known[12]. Therefore, under the present CITP conditions with excess of 1,10-phenanthroline, the majority of the Cu(II)– and Co(II)–phen chelate seems to be also present as $[Cu(phen)_2Cl]^+$ and $[Co(phen)_3]^{2+}$, respectively. These species will migrate thus maintaining the ligand-replacement and/or dissociation equilibria.

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