Liquid–Liquid Extraction and Liquid Chromatographic Studies on Interactions of Inorganic Anions with Coordinatively Unsaturated Copper(II) Complexes of Heterocyclic Azo Compounds

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The interactions between Cu(II) complexes with heterocyclic azo compounds and several anions were studied by equilibrium analysis of ion-pair extraction, RP-HPLC of metal complexes, and ion chromatography of anions on an ODS column coated with Cu(II) complexes of the long alkyl derivatives. Both ion-pair extraction and HPLC studies demonstrated that a dicationic complex with 8-(3,5-dibromo-2-pyridylazo)-5-aminoquinoline interacted with anions stronger than a monocationic complex with 2-(2-pyridylazo)methylphenol. Anions were more retained on the column coated with dicationic Cu(II) complex. Such differences were quantitatively ascribed to the first ion-pair formation of the dicationic complex giving a monocationic species.

Introduction

Heterocyclic azo compounds react with various metal ions to form stable complexes of high molar absorptivities and are widely used as precolumn derivatizing reagents in simultaneous determination of metal ions.[1,2] Among them, *o*-hydroxyheterocyclic azo compounds (HL) are monoanionic, tridentate ligands and form cationic complexes with cobalt and copper ions: $Co^{III}L_2^+$ and $Cu^{II}L^+$. Thus, appropriate salts are added so that these cationic complexes are retained in reversed-phase HPLC (RP-HPLC).[3-5] The cation of a salt interacted with residual silanol groups on the stationary phase to reduce the reactivity,[6] while the anion neutralized the charges on complexes to enhance the distribution. When 2-(4-methyl-2-quinolylazo)-5-diethylaminophenol was adopted as a derivatizing reagent, for example, the retentions of coordination-saturated $Co^{III}L_2^+$ were substantially the same irrespective of an additive like NH_4SCN and NH_4Br. In contrast, coordination-unsaturated $Cu^{II}L^+$ was appreciably retained with NH_4SCN but not with NH_4Br.[4] This suggested that a mixed ligand complex was formed in $Cu^{II}L^+$-SCN^-, while a simple ion-pair was formed in $Cu^{II}L^+$-Br^- and $Co^{III}L_2^+$-SCN^-, Br^-.

Generally, information obtained by partition or distribution of samples between two phases is useful to understand the HPLC behavior. Difficulties in equilibrium analysis of ion-pair extraction, however, have restricted such studies on charged species including cationic complexes. In this research, mixed-ligand complex and ion-pair formation behaviors were studied for a monocationic copper complex with 2-(2-pyridylazo)-methylphenol (PAC) and for a dicationic copper complex with 8-(3,5-dibromo-2-pyridylazo)-5-aminoquinoline (3,5-DiBr-PAAQ, R) to elucidate the effects of electric charges on complexes. First, we analyzed the equilibria on the ion-pair extraction of these complexes. Second, we examined the effects of anion on the retention of these complexes in RP-HPLC. Ion chromatography of anions on the supported metal complexes is another way to study the interaction. The retention of anions has been reported on the dicationic copper complex with *N,N*-bis(2-pyridylmethyl)octadecylamine,[7] but not on the monocationic complex. Thus, ion chromatographic behaviors of anions on an ODS column coated with copper complexes of their derivatives having a long alkyl chain, 2-(2-pyridylazo)-4-octyloxyphenol (PAOOP) and 8-(3,5-dibromo-2-pyridylazo)-5-octylaminoquinoline (3,5-DiBr-PAOAQ), were also examined. The results obtained by the three methods are compared and discussed.

Experimental

Reagents

Commercially available 2-(2-pyridylazo)-4-methylphenol was used as received.[8,9] 8-(3,5-Dibromo-2-pyridylazo)-5-aminoquinoline was courteously supplied by Prof. K. Ohshita (Daido Inst. Technol., Nagoya, Japan). One of the long alkyl derivatives, 2-(2-pyridylazo)-4-octyloxyphenol, was synthesized according to a previously reported method.[10] Another long alkyl derivative, 8-(3,5-dibromo-2-pyridylazo)-5-octylaminoquinoline, was synthesized by coupling 3,5-dibromo-2-aminopyridinediazonium salt with 5-octylaminoquinoline, which had been prepared by *N*-alkylation of 5-aminoquinoline with bromooctane in dimethylsulfoxide.[11] The crude compounds were purified by extraction with an acid and by column chromatography with silica-gel and hexane/ethyl acetate (67:33,

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v/v for PAOOP or 33:67, v/v for 3,5-DiBr-PAOAQ). Purities of the compounds were confirmed by ^{1}H NMR measured on a Model Gemini 300 spectrometer (300 MHz, Varian, CA) and by RP-HPLC. The distribution constant of PAC was determined to be $10^{3.7}$ from the pH dependence of the distribution ratio in alkaline media using pK_a of 8.9.[8] Each compound was dissolved in analytical-reagent grade ethanol to give a 2.5×10^{-4} mol dm^{-3} solution. Standard stock solutions (1.0×10^{-2} mol dm^{-3}, pH 2) of cobalt(II) and copper(II) were prepared by dissolving the analytical-reagent grade nitrates.   1-Octanol, 1-nonanol and octane were purified by extraction with sulfuric acid and sodium hydroxide solution.

Ion-pair extraction

In the extraction of PAC complexes, a 15-cm^3 portion of the solution containing 1×10^{-5} mol dm^{-3} copper(II), 5.0×10^{-5} mol dm^{-3} PAC, sulfuric acid (pH 4), 5.0×10^{-2} mol dm^{-3} ammonium sulfate and 4.0×10^{-6} – 0.8 mol dm^{-3} counter anion was added to a 15-cm^3 portion of 1-nonanol or 1-octanol/octane mixed solvent (30:70, v/v). In the extraction of 3,5-DiBr-PAAQ complexes, a 10-cm^3 portion of the solution containing 1×10^{-5} mol dm^{-3} copper(II), 1.5×10^{-5} mol dm^{-3} 3,5-DiBr-PAAQ, sulfuric acid (pH 3) and 2.0×10^{-4} – 0.4 mol dm^{-3} counter anion was added to a 10-cm^3 portion of 1-octanol. Two phases were shaken at 150 strokes/min for 30 min, and the pH of the aqueous phase was measured in the presence of an organic phase. After phase separation, the absorbance of an aqueous phase was measured to determine the concentration of the copper complex (Cu-PAC, 572 nm; Cu-3,5-DiBr-PAAQ, 571 nm). The concentration in the organic phase and the distribution ratio were calculated using this value.

Apparatus

The HPLC system (JASCO, Tokyo, Japan) consisted of a Model PU-980 intelligent pump, a Model 9725i sample injector with a 10-µl sample loop, a Model 965-CO column oven, a Model MD-915 multiwavelength UV-Vis detector (wavelength range 200 – 800 nm) equipped with a Model DP-L915 data processing system, and a Model CD-5 conductometric detector (Showa Denko, Tokyo, Japan). A Model L-column ODS (4.6 mm i.d. × 250 mm, particle diameter 5 µm; Chemical Evaluation Research Institute, Tokyo, Japan) was used for the separation of metal complexes with spectrophotometric monitoring. A Model Inertsil ODS-3 (4.0 mm i.d. × 100 mm, 3 µm; GL science, Tokyo, Japan) coated with a copper(II) complex was used for the separation of anions with conductometric monitoring.

Chromatographic procedure

All the chromatographic measurements were performed at a flow rate of 0.8 cm^3 min^{-1} and at a column temperature of 40˚C. In PAC complexes, a 1-cm^3 portion of an aqueous solution (pH *ca*. 4) containing 1×10^{-4} mol dm^{-3} of cobalt(II) and of copper(II) was added to 2-cm^3 of a 2.5×10^{-4} mol dm^{-3} ethanolic solution of PAC. The resulting solution was allowed to stand for at least 30 min. A 10-µl aliquot of the solution was placed on the column *via* an injection valve and eluted with acetonitrile/water containing 1×10^{-2} mol dm^{-3} NH$_4$SCN or NH$_4$Cl (pH *ca*. 6).   In the separation of 3,5-DiBr-PAAQ complexes, acetonitrile/water containing 1×10^{-2} mol dm^{-3} KSCN or KCl and 1×10^{-3} mol dm^{-3} sodium monochloroacetate (pH 3) was used as an eluent.

For the HPLC separation of anions on the column coated with a copper(II) complex, a 10-µl aliquot of 1×10^{-2} mol dm^{-3} NaCl, NaBr, NaSCN or NaClO$_4$ was placed on the column and eluted with 5×10^{-3} mol dm^{-3} sodium monochloroacetate solution.

The copper(II) complexes were coated as follows: the acetone–water solution (75:25, v/v, pH 3) of Cu(II)/PAOOP or Cu(II)/3,5-DiBr-PAOAQ (1:1, mol/mol) mixture was passed through an ODS column. After the absorbance of the eluent became constant, the coating was continued for 30 min to reach adsorption equilibria. Then, the column was removed from the chromatographic system, and the remaining parts were successively washed with acetone and water in order to replace the coating solution by the mobile phase without unfavorable deposition of the coating reagent. The coated column was set back into the system and was equilibrated with the mobile phase. The chemical amounts of copper complexes adsorbed on the column were spectrophotometrically determined after elution using acetone.

Results and Discussion

Ion-pair extraction of Cu(II) complexes

At pH 4, copper ion quantitatively reacts with PAC to form a monocationic 1:1 complex, CuL$^+$, which forms an ion-pair with an anion (A$^-$) in an aqueous phase:

$$CuL^+ + A^- \rightleftharpoons CuL^+ \cdot A^-, \quad K_{f1} = \frac{[CuL^+ \cdot A^-]}{[CuL^+][A^-]}$$
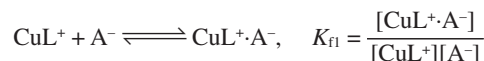
The product may be a mixed-ligand complex [CuLA] or an ion-pair CuL$^+$·A$^-$ depending on the coordinating ability of an anion. Since the equilibrium treatment is the same for these reactions, the product is tentatively expressed as an ion-pair.   The distribution of this ion-pair and the constant are expressed as:
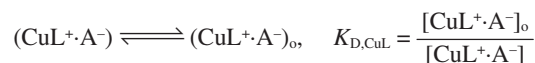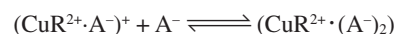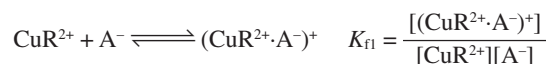
$$(CuL^+ \cdot A^-) \rightleftharpoons (CuL^+ \cdot A^-)_o, \quad K_{D,CuL} = \frac{[CuL^+ \cdot A^-]_o}{[CuL^+ \cdot A^-]}$$

The overall ion-pair extraction equilibrium and the constant are expressed as:

$$CuL^+ + A^- \rightleftharpoons (CuL^+ \cdot A^-)_o,$$

$$K_{ex,CuL} = \frac{[CuL^+ \cdot A^-]_o}{[CuL^+][A^-]} = K_{D,CuL}K_{f1}$$
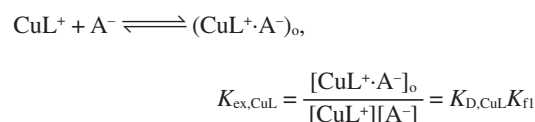
The distribution ratio of CuL$^+$, D_{Cu} can be expressed using these constants as:

$$D_{Cu} = \frac{[CuL^+ \cdot A^-]_o}{[CuL^+] + [CuL^+ \cdot A^-]} = \frac{K_{ex,CuL}[A^-]}{1 + K_{f1}[A^-]}$$

In contrast, the dicationic 1:1 complex with 3,5-DiBr-PAAQ, CuR^{2+} successively forms ion-pairs in two-steps:

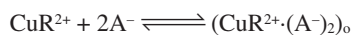$$CuR^{2+} + A^- \rightleftharpoons (CuR^{2+} \cdot A^-)^+ \quad K_{f1} = \frac{[(CuR^{2+} \cdot A^-)^+]}{[CuR^{2+}][A^-]}$$

$$(CuR^{2+} \cdot A^-)^+ + A^- \rightleftharpoons (CuR^{2+} \cdot (A^-)_2)$$

$$K_{f2} = \frac{[CuR^{2+} \cdot (A^-)_2]}{[(CuR^{2+} \cdot A^-)^+][A^-]}$$

The distribution of 1:2 ion pair and the constants are expressed as:
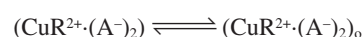
$$(CuR^{2+} \cdot (A^-)_2) \rightleftharpoons (CuR^{2+} \cdot (A^-)_2)_o$$

$$K_{D,CuR} = \frac{[CuR^{2+}\cdot(A^-)_2]_o}{[CuR^{2+}\cdot(A^-)_2]}$$

The overall ion-pair extraction equilibrium and the constants are expressed as:

$$CuR^{2+} + 2A^- \rightleftharpoons (CuR^{2+}\cdot(A^-)_2)_o$$

$$K_{ex,CuR} = \frac{[CuR^{2+}\cdot(A^-)_2]_o}{[CuR^{2+}][A^-]^2} = K_{D,CuR}\,K_{f1}\,K_{f2}$$

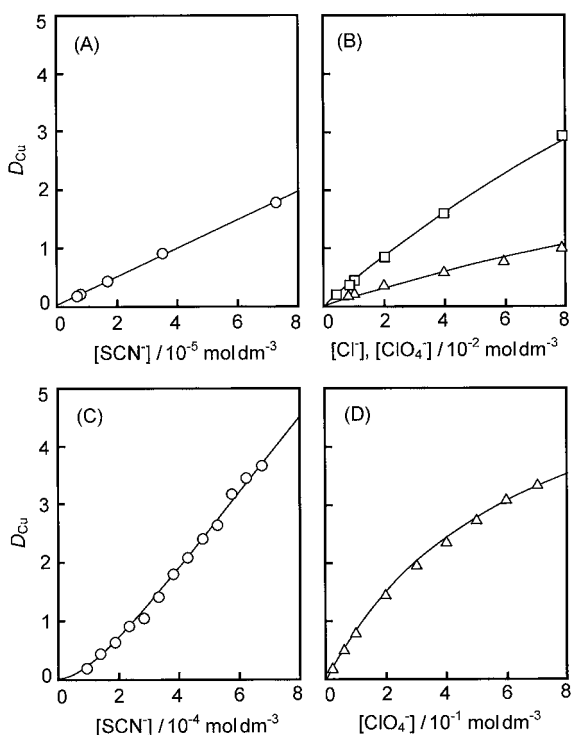The distribution ratio of CuR^{2+}, D_{Cu} can be expressed using these constants as:

Fig. 1 Equilibrium analysis on ion-pair extraction of copper(II) complexes of heterocyclic azo compounds with anions. Heterocyclic azo compound, organic phase: (A, B) PAC, 1-nonanol; (C, D) 3,5-DiBr-PAAQ, 1-octanol. Anion: ○, SCN⁻; □, Cl⁻; △, ClO₄⁻. The curves were calculated using the constants in Table 1.

$$D_{Cu} = \frac{[CuR^{2+}\cdot(A^-)_2]_o}{[CuR^{2+}] + [(CuR^{2+}\cdot A^-)^+] + [CuR^{2+}\cdot(A^-)_2]}$$

$$= \frac{K_{ex,CuR}[A^-]^2}{1 + K_{f1}[A^-] + K_{f1}K_{f2}[A^-]^2}$$

Since the concentration of an anion was much higher than that of the complex under the actual experimental conditions, the free concentration of an anion was assumed to be equal to the total concentration, $[A^-] = C_{A,w}$. The formation and distribution constants of ion-pairs were determined so as to give the best agreement between the experimental and calculated distribution ratios in each reaction system. Figure 1 shows the plot of D_{Cu} vs. $[A^-]$ for several reaction systems, while Table 1 summarizes the constants. The calculated curves using the constants in Table 1 could reproduce the experimental points. Microsoft Excel® was used for data analysis.

1-Octanol giving moderate distribution ratios was mainly used as an organic phase, while 1-nonanol or 1-octanol/octane mixture was also adopted in case of high extractability. Even with these solvents, the extractability of CuL^+ in the presence of SCN^- was too high for equilibrium analysis. Since the 1:2 ion-pair of CuR^{2+} was not formed in an aqueous phase containing Cl^- or Br^-, only the product of $K_{D,CuR}K_{f2}$ was available. The K_{f1} values of CuL^+ in the presence of varying anions are comparable to each other and are relatively small ($10^{0.4}$ – $10^{0.7}$), while those of CuR^{2+} are much larger. This is ascribed to the difference in charge of the metal complexes. The K_{f1} values of CuR^{2+} are even larger than those of Cu^{2+} aqua ion (10^0 (Cl^-), $10^{-0.1}$ (Br^-), $10^{1.9}$ (SCN^-), $I = 0.5$)[12] by two-orders of magnitude; hydrophobic interaction may thus contribute. The K_{f2} value of CuR^{2+} in the presence of ClO_4^- is smaller than the K_{f1} value by 2.5 orders of magnitude; this is characteristic for stepwise ion-pair formation of multivalent ions. In contrast, the K_{f2} value of CuR^{2+} in the presence of SCN^- is rather comparable to the K_{f1} value; this is characteristic for stepwise complex formation.

RP-HPLC behaviors

The chromatograms of metal ions derivatized with PAC or 3,5-DiBr-PAAQ on an ODS column are shown in Fig. 2, using 1.0×10^{-2} mol dm⁻³ NH_4SCN or NH_4Cl solution in acetonitrile/water (60:40 or 40:60, v/v) as a mobile phase. A fully end-capped ODS column was employed. With use of PAC at pH ca. 6, the retention of coordinatively unsaturated CuL^+ was markedly enhanced and the peak profile was improved in the presence of SCN^- (Fig. 2(A)) than in the presence of Cl^-

Table 1   Parameters on ion-pair extraction of copper complexes

Reagent	Complex	Solvent	Counter anion	$\log K_{ex}$	$\log K_D$	$\log K_{f1}$	$\log K_{f2}$	$\log(K_DK_{f2})$
PAC	CuL^+	1-Nonanol	Cl^-	1.6	1.1	0.5		
			Br^-	1.7	1.1	0.6		
			SCN^-	4.4	(2.3)[a]	(2.1)[a]	—	—
			ClO_4^-	1.2	0.8	0.4		
		1-Octanol/octane (30:70, v/v)	Cl^-	0.7	0.1	0.6		
			Br^-	1.0	0.3	0.7		
			SCN^-	3.3	n.d.	n.d.	—	—
			ClO_4^-	n.e.	n.e.	n.e.		
3,5-DiBr-PAAQ	CuR^{2+}	1-Octanol	Cl^-	4.2	—	2.7	—	1.5
			Br^-	4.1	—	2.0	—	2.1
			SCN^-	7.5	1.8	3.6	2.1	3.9
			ClO_4^-	3.6	0.8	2.7	0.2	1.0

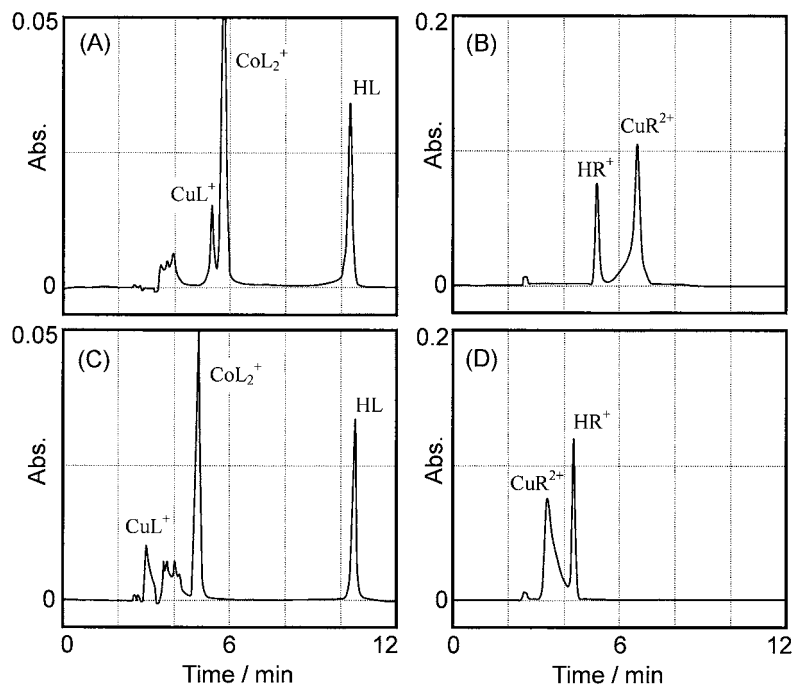n.d., Not determined separately; n.e., no extraction. a. See text for details.

Fig. 2 Chromatograms of cationic complexes with heterocyclic azo compounds. Column, L-column ODS; eluent, acetonitrile–water containing 1×10^{-2} mol dm^{-3} SCN$^-$ [(A), (B)] or Cl$^-$ [(C), (D)]. Flow-rate: 0.8 cm^3 min^{-1}. Column temperature: 40°C. Ligand: (A), (C), PAC; (B), (D), 3,5-DiBr-PAAQ. Acetonitrile (%, v/v): 60 (PAC); 40 (3,5-DiBr-PAAQ).

(Fig. 2(C)) due to mixed-ligand complex formation. In contrast, the retention of CoL$_2^+$ was slightly enhanced in the presence of SCN$^-$ compared with Cl$^-$; this is ascribed to the difference in lipophilicity of a counter ion in an ion-pair distributed into an ODS phase.

The effects of an anion concentration on the retentions were studied. The intrinsic retention factor of an ion-pair of (CuL$^+$·A$^-$) was obtained at a lower concentration for SCN$^-$ than for Cl$^-$, as reported for a related compound.[4] The distribution constant of (CuL$^+$·SCN$^-$) is reasonably estimated to be 10$^{2.3}$, based on the linear correlation between the logarithm of the intrinsic retention factors (–0.26 for CuL$^+$·Cl$^-$, –0.26 for CuL$^+$·Br, 0.49 for HL, and 0.07 for CuL$^+$·SCN$^-$ with acetonitrile/water as a mobile phase) and the logarithmic distribution constants (1.1 for CuL$^+$·Cl$^-$, 1.1 for CuL$^+$·Br$^-$, and 3.7 for HL at nonanol/water). The ion-pair formation constant of (CuL$^+$·SCN$^-$) may be evaluated to be 10$^{2.1}$ as shown in the parentheses on Table 1.

With use of 3,5-DiBr-PAAQ at pH 3, the retention of CuR^{2+} was enhanced in the presence of SCN$^-$ compared with Cl$^-$ (Figs. 2(B), (D)), and the enhancement was more marked than in the case of PAC. Since the free concentration of monochloroacetate was estimated to be as low as 7.3×10^{-4} mol dm^{-3}, the retention of metal complexes was not influenced. Although a related reagent of 2-(8-quinolylazo)-4,5-diphenylimidazole was studied as a precolumn derivatizing reagent for the separation of Cd, Zn, Ni, and Co at pH 7.5, the copper complex was not detected as a peak.[13] The stable species at such pH was CuR$_2^{2+}$, which gradually dissociated after separation from an excess ligand. The retention of a free ligand was also slightly enhanced in the presence of SCN$^-$, due to more favorable distribution of the cationic species (HR$^+$, pK_a 4.1).

Ion chromatography of anions on ODS columns coated with copper complexes

Ion chromatographic behaviors of anions were studied on ODS columns coated with Cu(II) complexes of corresponding derivatives with a long alkyl chain. The logarithmic retention factors of anions on the column coated with Cu-PAOOP complex are plotted against the logarithmic concentration of monochloroacetate in Fig. 3. A linear relationship with a slope of –1 was observed for all the anions.

The retention factors of anions on the charged metal complexes immobilized on the column were reported to be approximated by:[7]

$$k = \left\{ \frac{K_{ex}\text{Cap}}{[\text{E}^-]} \right\} \left[\frac{w}{v_0} \right],$$

where K_{ex}, E, Cap, w and v_0 are an anion-exchange constant, an eluting anion, an anion exchange capacity of packing material, a mass of packing material in a column, and a void volume of a column, respectively. Since Cap, w and v_0 are constant, the intercepts of lines in Fig. 3 reflected the affinities of anions relative to an eluent. The difference in intercept between SCN$^-$ and Cl$^-$ is about 1.3, which agrees with the difference in log K_f determined by ion-pair extraction and HPLC (2.1 – 0.5 = 1.6).

With an increase in concentration of a coating reagent, the chemical amounts of the complexes adsorbed on the column were linearly increased. The adsorbed amount of 3,5-DiBr-PAOAQ complex was smaller than that of PAOOP complex. The retentions of anions linearly increased with an increase in adsorbed amount of the complex as shown in Fig. 4. At the same coated amount of 2.0×10^{-7} mol, anions were more retained by 3,5-DiBr-PAOAQ complex than by PAOOP complex. This agrees with that, in the equilibrium analysis of ion-pair extraction using Cu(II) complexes with corresponding
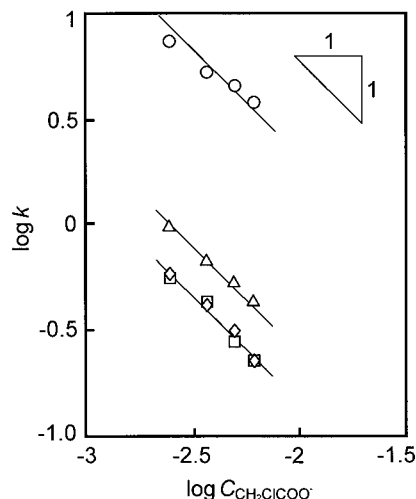
Fig. 3   Logarithmic retention factors of anions on column coated with PAOOP complex plotted against logarithmic concentration of monochloroacetate. Column, Inertsil ODS-3; coated amount, 1.2×10^{-6} mol; eluent, $CH_2ClCOOH$–NaOH (pH 3). Flow-rate: 0.8 cm^3 min^{-1}. Column temperature: 40°C. Anion: △, ClO$_4^-$; ○, SCN$^-$; ◇, Br$^-$; □, Cl$^-$.
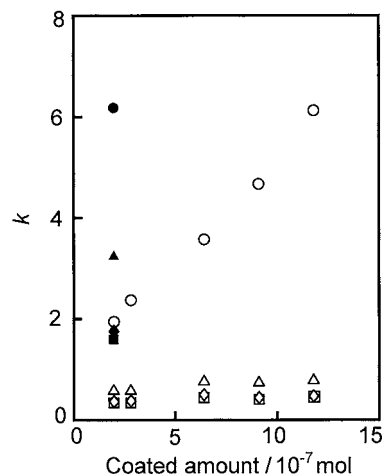

Fig. 4   Retention factors of anions on columns coated with cationic copper(II) complexes. Column, Inertsil ODS-3; eluent, 5.0×10^{-3} mol dm^{-3} $CH_2ClCOOH$–NaOH (pH 3). Flow-rate: 0.8 cm^3 min^{-1}. Column temperature: 40°C. Reagent: open symbols, PAOOP; closed symbols, 3,5-DiBr-PAOAQ. Anion: △, ▲, ClO$_4^-$; ○, ●, SCN$^-$; ◇, ◆, Br$^-$; □, ■, Cl$^-$.

ligands, K_{f1} or K_{ex} of 3,5-DiBr-PAAQ is larger than that of PAC (Table 1). The adsorbed amount of PAOOP complex giving the retention factor (*ca.* 6) of SCN$^-$ comparable to that with 2.0×10^{-7} mol of 3,5-DiBr-PAOAQ complex was as much as 1.2×10^{-6} mol, where the retentions of Cl$^-$, Br$^-$ and ClO$_4^-$ were substantially identical to each other and were smaller compared with those on the column coated with 3,5-DiBr-PAOAQ complex.

Conclusions

Ion-pair formation or mixed-ligand complex formation behaviors were studied for a monocationic copper complex with PAC and for a dicationic copper complex with 3,5-DiBr-PAAQ by equilibrium analysis on ion-pair extraction, by RP-HPLC of metal complexes. The distribution constants of (CuL$^+$·A$^-$) were comparable to those of (CuR^{2+}·(A$^-$)$_2$). Moreover, the ion-pair formation constants of (CuL$^+$·A$^-$) ($K_{f1} = 10^{0.4}$ for ClO$_4^-$; $10^{2.1}$ for SCN$^-$) were substantially the same as the second ion-pair formation constants of (CuR^{2+}·(A$^-$)$_2$) ($K_{f2} = 10^{0.2}$ for ClO$_4^-$; $10^{2.1}$ for SCN$^-$). Thus, the extractabilities of (CuR^{2+}·(A$^-$)$_2$) were higher than those of (CuL$^+$·A$^-$) by the first ion-pair formation. Such higher affinities of CuR^{2+} to anions, especially to SCN$^-$, were reflected in the higher retentions of anions in ion chromatography using 3,5-DiBr-PAOAQ.

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