

Determination of Formation and Partition Constants of Ion Associates in Extraction of Cationic Cobalt(III) Complexes with Pyridylazo Compounds.

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The extractions of cationic cobalt(III) complexes with four kinds of pyridylazo compounds using alcohol or chloroform were carried out. The formation and partition constants of ion associates formed with the cationic cobalt(III) complex and a counter anion (ClO_4^- , SCN^- , Br^- , Cl^-) were determined by an analysis of the extraction equilibria. By using 1-nonanol instead of 1-octanol as the organic solvent, the formation constants of ion associates increased ($\Delta \log K_f \approx 0.4$), while their partition constants decreased ($\Delta \log K_D \approx -0.3$) in all present systems. Moreover, only in the 4-methyl-2-(2-pyridylazo)phenol (PAC) system, the formation constant for the chloride ion system ($\log K_f = 1.7$) was observed to be greater than that for the bromide ion system ($\log K_f = 1.0$). The formation constants of ion associates were found to be mostly dependent on the bulkiness and the polarity of the pyridylazo compounds. These results provide fundamental information on the retention behaviours of cationic complexes in the RP-HPLC.

(Received on August 9, 2001; Accepted on September 13, 2001)

Pyridylazo compounds are useful reagents for analysis of metal ions and a variety of derivatives have been prepared to modify the selectivity and to enhance the sensitivity.¹ These act as a tridentate ligand and form stable complexes with various metal ions except for alkali and alkaline earth metal ions.

The diversity in chemical properties (electric charge and composition) and inertness of the resulting complexes enable their use as a precolumn derivatizing reagent for simultaneous determination of metal ions using reversed-phase high-performance liquid chromatography (RP-HPLC).²⁻¹⁰

Previously,¹¹ we have studied the chromatographic behaviors of metal complexes with 1-(2-Pyridylazo)-2-naphthol (HL as a neutral form). Four metal ions could be separated on an ODS column using acetonitrile–water (70:30, v/v) containing $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ammonium thiocyanate as a mobile phase. The elution order was $\text{Cu}^{\text{II}}\text{L}^+ < \text{Co}^{\text{III}}\text{L}_2^+ \ll \text{HL} < \text{NiL}_2 < \text{Fe}^{\text{II}}\text{L}_2$. On the other hand, when methanol–water or acetone–water system was used as mobile phase, the elution order of $(\text{Co}^{\text{III}}\text{L}_2)^+\text{SCN}^-$ and $(\text{Cu}^{\text{II}}\text{L})^+\text{SCN}^-$ is reversed. It is suggested that the retention of $(\text{Co}^{\text{III}}\text{L}_2)^+\text{SCN}^-$ selectively decrease among all complexes, but the retention mechanism of these ion associates from mobile phase to stationary phase was not examined in detail.

The ion association extraction is very useful technique to resolve this problem. In the ion association extraction, a given ionic species forms an ion association complex with counter ion in the aqueous phase and subsequently the complex partitions to the organic phase. Then, ion association extraction is dependent on the formation constant of the ion association complex and its partition constant.

The extraction constant, which is defined as the product of the formation constant in the aqueous phase and the partition constant of the ion associate, were investigated in detail.¹²⁻¹⁹ However, these individual formation and partition constants are

scarcely determined, because it is difficult to determine the formation constant.

In our previous work, the formation constants of 2-(2-pyridylazo)-1-naphthol-4-sulfonate and its anionic copper(II) complex with tetrabutylammonium ion in the aqueous phase and their partition constants could be estimated by an analysis of the partition equilibrium.²⁰

In the present work, we have carried out the ion association extractions of cationic cobalt(III) complexes with four kinds of pyridylazo compounds using alcohol or chloroform as organic phase and have determined the formation and partition constants of ion associates. The electrostatic and hydrophobic properties of the cationic cobalt(III) complexes influenced the formation of ion associate. Only in the 4-methyl-2-(2-pyridylazo)phenol (PAC) system, the formation constant for the chloride ion system was observed to be greater than that for the bromide ion system. The structure of Co(III)-PAC complex is shown in Fig. 1.

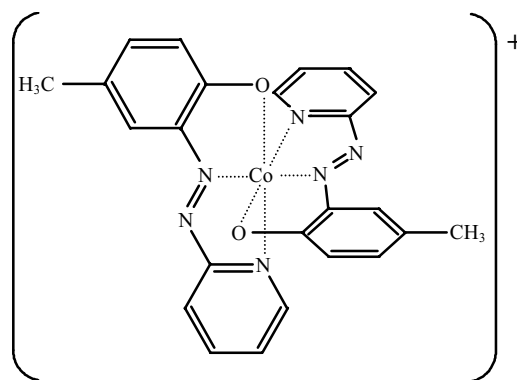


Fig. 1 The structure of $\text{Co}^{\text{III}}\text{L}_2^+$ (L: PAC)

Experimental

Reagents

PAC, 5-dimethylamino-2-(2-pyridylazo)phenol (PAM), 5-(2-pyridylazo)-6-hydroxyquinoline (PA6HQ) and 7-(2-pyridylazo)-8-hydroxyquinoline (*o*-PAHQ), synthesized in our laboratory previously, were dissolved in ethanol to give $1.5 \times 10^{-3} \text{ mol dm}^{-3}$ solutions. Octane of reagent grade was purified by washing successively with concentrated sulfuric acid, dilute sodium hydroxide, dilute perchloric acid solutions and water. 1-Octanol and 1-nonanol of reagent grade were purified by a similar method as octane, except for not using concentrated sulfuric acid. Chloroform of reagent grade was purified by washing successively dilute sodium hydroxide and water. Cobalt(II) standard solution was prepared from cobalt(II) sulfate heptahydrate (99%, Wako Pure Chemical Industries Ltd., Osaka, Japan). All other reagents were of reagent grade and were used without further purification. The water used was purified by means of a Toraypure LV-10T ultrapure water manufacturing device (Toray Industries Inc., Tokyo, Japan).

Procedure

A 5 ml portion of $3.0 \times 10^{-5} \text{ mol dm}^{-3}$ cobalt(II) solution was placed in a 50-ml centrifuge tube and mixed with 0.5 ml of $1.5 \times 10^{-3} \text{ mol dm}^{-3}$ chelating reagent solution, and the solution were allowed to stand for at least 30 min. Further, 1 ml of $2.5 \times 10^{-3} \text{ mol dm}^{-3}$ sulfuric acid solution for pH adjustment, 2.5 ml of 0.30 mol dm^{-3} ammonium sulfate solution for an adjustment to ionic strength and a proper amount of counter anion solution were added, then the mixture was diluted with water until the total volume of solution was 15 ml (pH ca. 4). The resulting aqueous phase was shaken with 15 ml of organic phase for 30 min, which was sufficient for complete equilibration. Partition was performed in a thermostatic bath kept at 25 °C. After centrifuging for 5 min at 3000 rpm, the concentration of the cobalt(III) complex in the aqueous phase was determined by measuring the absorbance at the wavelength of its absorption maximum in a 1-cm cell against water. The concentration of the cobalt(III) complex in the organic phase was determined by deducing that in the aqueous phase from the initial concentration of cobalt(II), $1.0 \times 10^{-3} \text{ mol dm}^{-3}$.

Apparatus

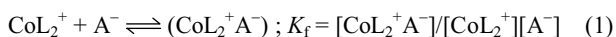
A Shimadzu UV-2200A spectrophotometer was used for spectrophotometric measurements. pH measurements were made with a DKK COM20 pH meter equipped with a Horiba 6028-10T glass combination pH electrode. The other apparatus were the same as those used in a previous study for mechanical shaking and centrifugation.

Results and Discussion

Analysis of extraction equilibrium on cationic Co(III) complex

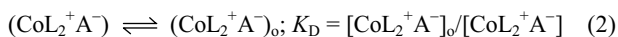
The partition equilibrium of ion associates of cationic Co(III) complex with counter anion is dependent on the following two kinds of equilibria.

Ion association of cationic Co(III) complex with counter anion in the aqueous phase:



where A^- denotes the counter anion.

Partition of the ion associates:



where the subscript o refers to the organic phase.

The overall extraction equilibrium and the extraction constant are expressed as:



The partition ratio of Co(III) complex in the present systems can be written as:

$$D = \frac{[\text{CoL}_2^+\text{A}^-]_o}{[\text{CoL}_2^+] + [\text{CoL}_2^+\text{A}^-]} \quad (4)$$

From equations (1), (3) and (4), the following relation can be obtained:

$$D = \frac{K_{\text{ex}} [\text{A}^-]}{1 + K_f [\text{A}^-]} \quad (5)$$

Taking logarithms of Eq. (5),

$$\log [\text{A}^-] - \log D = \log (1 + K_f [\text{A}^-]) - \log K_{\text{ex}} \quad (6)$$

Under the condition $C_{\text{A,w}} \gg C_{\text{CoL}_2^+}$ ($C_{\text{A,w}} = C_{\text{A}} - [\text{CoL}_2^+\text{A}^-]_o$) in the aqueous phase, the above equation can be further approximated as

$$\log C_{\text{A,w}} - \log D = \log (1 + K_f C_{\text{A,w}}) - \log K_{\text{ex}} \quad (6')$$

By replacing left-hand side of Eq. (6)' with Y and $K_f C_{\text{A,w}}$ with X , the equation is equivalent to $Y = \log (1+X)$. Then, according to Eq. (6)', plots of $\log C_{\text{A,w}} - \log D$ against $\log C_{\text{A,w}}$ should be superimposable on the normalized curve, $\log (1+X)$ vs. $\log X$, and the values of K_{ex} and K_f can be estimated from the respective deviations of the ordinate and abscissa between the plots and the normalized curve. As an example, the results for 1-nonanol-PAC-SCN system are shown in Fig. 2.

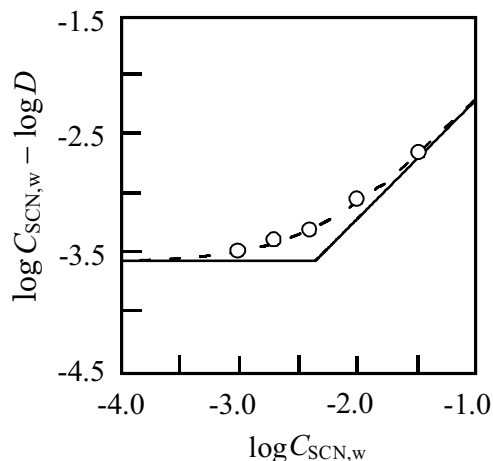


Fig. 2 Determination of the formation and partition constants of Co(III)-PAC complex with SCN^- . The dotted curve is the normalized curve, $\log (1+X)$ vs. $\log X$, and the solid lines are the asymptotes of the normalized curve.

The validity of the present approximation for the concentration of the counter anions

In the present work, we adopted $[\text{A}^-] = C_{\text{A,w}}$ as a approximation. To confirm that the counter anions were not extracted into the organic phase without the cationic Co(III) complexes, the following operation was performed. The aqueous phase (15 ml), which was prepared by the similar procedure to that described above, except for not containing cobalt and chelating reagent, was shaken with 15 ml of organic phase for 30 min. After centrifuging for 5 min, an aliquot (10 μl) of the aqueous phase was subjected to ion

chromatography. The elution of the anion was monitored by a conductometric detector. A Waters SPHERISORB SAX-5 (4.6 mm i.d. x 150 mm) was used as anion-exchange column. The mobile phase was the aqueous solution containing 5.0×10^{-3} mol dm^{-3} phthalic acid and 5.0×10^{-3} mol dm^{-3} tris(hydroxymethyl)aminomethane buffer (pH ca. 4). The calibration curves based on peak area for each anion were linear in the range 1.0×10^{-3} – 1.0×10^{-2} mol dm^{-3} . From this investigation, the concentration of the counter anion in the respective aqueous phase shaken with the organic phase was found to be equal to that in the aqueous phase not shaken with the one. It was proven that the counter anions were not extracted into the organic phase without the cationic Co(III) complexes.

Furthermore, the change in the absorption spectra for the Co(III) complexes with increasing in the concentration of the counter anion in aqueous phase was examined. Any change in the absorption spectra was not observed in all chelating reagent systems. Hence, the present approximation was confirmed to be valid for the analysis of extraction equilibrium on these Co(III) complex systems.

Effects of organic solvents on the extraction of cationic Co(III) complex

In this work, three kinds of organic solvents such as chloroform, 1-octanol and 1-nonanol were examined as organic phase. In PAM systems, these solvents were suitable for the analysis of extraction equilibrium. Chloroform and 1-octanol were unfit for the extraction of PAC and PA6HQ complexes because of its considerably high extractability. On the other hand, when 1-octanol and 1-nonanol were used, *o*-PAHQ complex was not extracted except for the thiocyanate system owing to its low extractability.

In PAM–chloroform or PAC–1-nonanol– ClO_4^- or PA6HQ–1-nonanol– SCN^- systems, the values of K_D and K_f could not be estimated. This suggested that the partition of these ion associates are too large to estimate the formation constant. In *o*-PAHQ–1-octanol– SCN^- system, the precise analysis could not be carried out, because the reproducible partition ratios were not obtained at $C_{\text{SCN}^-} > 0.1$ mol dm^{-3} .

The extraction constants (K_{ex}), the formation constants (K_f) and the partition constant (K_D : K_{ex}/K_f) estimated by an analysis of the partition equilibrium of each pyridylazo complexes systems were summarized in Tables 1 – 4.

Table 1 The extraction, partition and formation constants of Co(III)-PAC complex

Solvent	Counter anion	$\log K_{\text{ex}}$	$\log K_D$	$\log K_f$
1-nonanol	ClO_4^-	3.0	–	–
	SCN^-	3.6	1.3	2.3
	Br^-	2.3	1.3	1.0
	Cl^-	2.5	0.8	1.7

Table 2 The extraction, partition and formation constants of Co(III)-PAM complex

Solvent	Counter anion	$\log K_{\text{ex}}$	$\log K_D$	$\log K_f$
Chloroform	ClO_4^-	4.7	–	–
	SCN^-	4.3	–	–
	Br^-	2.6	–	–
	Cl^-	1.4	–	–
1-nonanol	ClO_4^-	1.4	0.3	1.1
	SCN^-	1.8	0.3	1.5
	Br^-	0.6	–0.1	0.7
	Cl^-	0.0	0.0	0.0
1-octanol	ClO_4^-	1.3	0.6	0.7
	SCN^-	1.7	0.6	1.1
	Br^-	0.3	0.3	0.0
	Cl^-	0.1	–	–

Table 3 The extraction, partition and formation constants of Co(III)-PA6HQ complex

Solvent	Counter anion	$\log K_{\text{ex}}$	$\log K_D$	$\log K_f$
1-nonanol	ClO_4^-	2.6	1.3	1.3
	SCN^-	2.8	–	–
	Br^-	1.6	0.8	0.8
	Cl^-	1.0	0.8	0.2

Table 4 The extraction, partition and formation constants of Co(III)-*o*-PAHQ complex

Solvent	Counter anion	$\log K_{\text{ex}}$	$\log K_D$	$\log K_f$
Chloroform	ClO_4^-	4.9	1.4	3.5
	SCN^-	4.3	1.4	2.9
	Br^-	2.5	1.0	1.5
	Cl^-	0.8	–0.2	1.0
1-nonanol	SCN^-	0.4	0.0	0.4
1-octanol	SCN^-	0.7	–	–

As can be seen in *o*-PAHQ system (Table 4), by using alcohols as the organic phase, the extraction constants for the thiocyanate systems got significantly smaller compared with the system using chloroform. That was expected from the difference in dielectric constant of these solvent. However, from the results in the 1-nonanol system, it has been noted that the cause of the decrease in the extraction constant was found to be decrease in the formation constant as well as that in the partition constant.

In PAM system (Table 2), appreciable difference in extraction constants for each anion system was not observed between 1-nonanol and 1-octanol systems. However, by using 1-nonanol system instead of 1-octanol system, the formation constants of ion associates increased ($\Delta \log K_f \approx 0.4$), while their partition constants decreased ($\Delta \log K_D \approx -0.3$), is shown in Table 2. This suggests that 1-octanol in aqueous phase may disturb the formation of ion associates.

Effects of counter anions on the extraction of cationic Co(III) complex

In PAM or *o*-PAHQ systems (Table 2 or 4), the extraction constants of the respective ion associates decrease in the order of $\text{ClO}_4^- > \text{SCN}^- > \text{Br}^- > \text{Cl}^-$ in the chloroform systems, which was expected from the order of lipophilicity of the counter anion. On the other hand, by using 1-nonanol as a solvent, the order of ClO_4^- and SCN^- was reversed (Table 1, 2 or 3). As can be seen in PAM system (Table 2), the difference in these extraction constants can be attributed to the formation constants.

Moreover, only in PAC system (Table 1), the formation constant for the chloride ion system ($\log K_f = 1.7$) was observed to be greater than that for the bromide ion system ($\log K_f = 1.0$). The ion association of Co(III)–PAC complex may be based on electrostatic interaction as well as hydrophobic one.

Contributions of formation constants to extraction constants.

Figure 3 shows the extraction constants, the formation constants and the partition constants obtained by using the *o*-PAHQ–chloroform and PAM–1-nonanol system.

As can be seen in Fig. 3, the contributions of formation constants to the extraction constants are greater than that of the partition constants irrespective of a type of the chelating reagents. In our previous RP-HPLC,¹¹ the concentration of the salts in the mobile phase is 1.0×10^{-2} mol dm^{-3} , then, the effects of ion association may be not reduced at this concentration. This results is very important in the discussion about the retentions of cationic complexes.

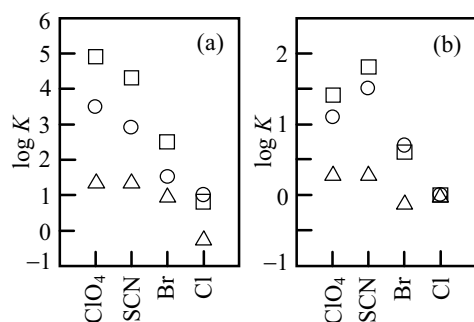


Fig. 3 Effect of counter anion on the extraction, formation and partition constants. (a) *o*-PAHQ-chloroform systems, (b) PAM-1-nonanol systems; (□) K_{ex} , (○) K_f , (△) K_D .

Effects of chelating reagents on the extraction of cationic Co(III) complex

Figure 4 shows the formation and partition constants for three kinds of chelating reagent systems obtained by using the 1-nonanol as a solvent. The partition constants for PAM systems were smaller than that for the others. This is explained by the difference in lipophilicity of the substituents group introduced into the phenol ring. While, the formation constants for PAM systems were not appreciably different from those for PA6HQ systems. The electrostatic interaction between the cationic complex and the counter anion may be dominant over the hydrophobic one.

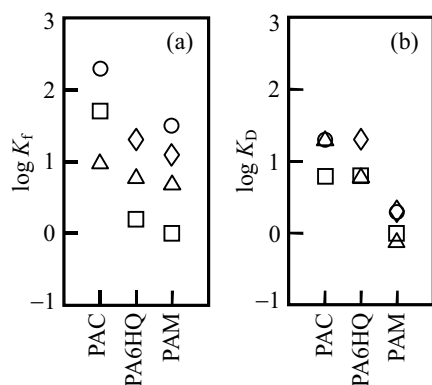


Fig. 4 Effect of chelating reagent on the formation constants (a) and partition constants (b) (1-nonanol systems). (◇) ClO₄, (○) SCN, (△) Br, (□) Cl.

In the analysis of extraction equilibria for the cationic cobalt(III) complexes with pyridylazo compounds, 1-nonanol was found to be most useful solvent for the determination of the formation and partition constants of ion associates. 1-Nonanol gave an appropriate partition constant for these ion associates.

The formation constants for the 1-nonanol systems may be smaller than the net values because 1-nonanol dissolved in aqueous phase disturbs the formation of ion associates.

The partition constants of the ion associates were depended on the polarity of the pyridylazo compounds, while the formation constants of ion associates were found to be mostly depended on the bulkiness of the pyridylazo compounds. These results provide fundamental information on the retention of the cationic complexes in the RP-HPLC.

Acknowledgements

The present work partially supported by the Grant-in-Aid for Scientific Research (No. 12640585) from the Ministry of Education, Science, Sports and Culture, Japan.

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