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Ion-pair extraction of Am(III) and Eu(III) with oligo-pyridine ligand

Ken-ichiro Ishimori [a,*], Masayuki Watanabe [a], Takaumi Kimura [a],
Masaki Murata [b], Hiroshi Nishihara [b]

[a] *Department of Materials Science, Japan Atomic Energy Research Institute, Tokai-mura Ibaraki, 319-1195, Japan*
[b] *Department of Chemistry, School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*

Abstract

The ion-pair extraction of Am(III) and Eu(III) using tris(2-pyridyl)carbinol (TPC) and tris(2-pyridyl)methoxymethane (TPM) was studied. The distribution ratio of Am(III) and Eu(III) was improved by the addition of TPC or TPM in the presence of picric acid (Hpic) as ion-pair reagent. In chloroform, 1,2-dichloroethane and nitrobenzene systems, the extraction of Am(III) and Eu(III) shows a moderate selectivity of Am(III) over Eu(III). In present study, the extraction equilibrium of Am(III) and Eu(III) with TPC and Hpic was investigated in detail, in order to elucidate the extraction property of TPC. On the extraction of Am(III) and Eu(III) with TPC and Hpic into 1,2-dichloroethane, three molecules of TPC coordinate to respective trivalent ions (M^{3+}). The extraction equilibrium was found as follows; $M^{3+} + 3TPC + 3pic^- \leftrightharpoons M(TPC)_3(pic)_{3,org}$. The extraction constants were $10^{15.99}$ for Am(III) and $10^{15.06}$ for Eu(III).

Keywords: Americium(III); Europium(III); Solvent extraction; Oligo-pyridine ligand; Separation factor

1. Introduction

The use of nitrogen-based soft-donor ligands, such as terpyridine [1], has drawn current attention in the field of the separation of trivalent actinides from lanthanides [2], because soft-donor ligands have stronger affinity to trivalent actinide than to lanthanide. A strategy of the successful ligand design for the separation is to use multidentate ligand containing soft-donors. Oligo-pyridine ligand with multiple soft-donor sites is competent for this strategy. An oligo-pyridine ligand, tris(2-pyridyl)carbinol (TPC) (Fig. 1) has a variety of coordination modes with three nitrogen-donors on pyridine rings and an oxygen-donor on the alkoxy group. The spectral and structural studies for TPC complexes of cobalt(III [3], II [4]), nickel(II) [4], iron(II) [4], ruthenium(II) [5] and monomethylindium(III)[6] have been reported and have found that TPC possesses a couple of coordination modes, i.e., N, N′, N″ and N, N′, O modes, with the metal ions. Recently trivalent lanthanide complexes, which contain TPC have been successfully synthesized and structurally identified as alkoxy-bridged-dinuclear complexes by X-ray crystallography [7]. However, the solvent extraction of metal ions using TPC has never been reported. It would be of a great interest to investigate the extraction of Am(III) and Eu(III) with TPC and clarify the coordination mode in the solvent extraction. Ion-pair extraction system by using the ligand in combination with hydrophobic counter anion possessing low donating ability such as picrate anion is expected to bring out the potentiality of the ligand as soft-donor for the separation of Am(III) and Eu(III). In addition, methoxy derivative of TPC, tris(2-pyridyl)methoxymethane (TPM) (Fig. 1), might be anticipated as more effective soft-donor ligand on the solvent extraction of Am(III) and Eu(III) because the methoxy substituent inhibits the coordination based on oxygen atom. In this study, ion-pair extraction of Am(III) and Eu(III) with TPC and TPM in the presence of picric acid (Hpic) as counter reagent was carried out and a detailed study on the extraction equilibrium of Am(III) and Eu(III) was investigated in TPC-Hpic-1,2-dichloroethane system in order to elucidate the extraction equilibrium.

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* Corresponding author. Tel.: +81 29 282 6723; fax: +81 29 282 6723.
E-mail address: ishimori@popx.tokai.jaeri.go.jp (K.-i. Ishimori).

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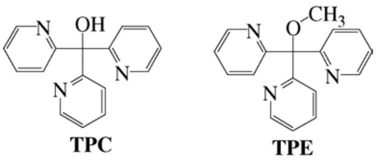

Fig. 1. Structural formula of oligo-pyridine ligands.

2. Experimental

2.1. Reagents

Stock solutions of ^{241}Am(III) and ^{152}Eu(III) were prepared by diluting the respective carrier-free radioisotopes with 1.0×10^{-3} mol dm^{-3} nitric acid. Unless otherw specified, these tracer solutions were used for solvent extraction.

Tris(2-pyridyl)carbinol and tris(2-pyridyl)methoxymethane were synthesized and purified by previously reported method [8,9]. TPC was recrystallized from acetonitrile. TPM was purified by silica-gel column chromatography with triethylamine–ethyl acetate (1:99, v/v) as eluent, and then recrystallized from acetonitrile. TPC and TPM were identified by liquid chromatography–electrospray ionization mass spectrometry in positive mode with octadecyl/silica-gel column. The high purities (>99.7%) of TPC and TPM were checked from peak area on the chromatogram at wavelength 260 nm of UV–vis detector. Chloroform (Wako, GR) was washed with water several times just before use to remove a stabilizer. Water was purified with a Milli-Q (Millipore) equipment just before use. Other reagents were of guaranteed reagents grade and used without further purification.

2.2. Measurement of distribution ratio of oligo-pyridine ligands

A 1,2-dichloroethane solution of $(0.010–1.0) \times 10^{-2}$ mol dm^{-3} oligo-pyridine ligand (L; TPC or TPM) was shaken for 10 min with an equal volume of an aqueous solution at pH 1.37–7.73 and 25.0 ± 0.5 °C. The ionic strength (I) of the aqueous phase was adjusted to 1.0×10^{-1} mol dm^{-3} with sodium nitrate and nitric acid. After centrifugation, the pH of the aqueous phase was measured with a glass electrode to calculate the H$^+$ concentration from the equilibrium pH and the activity coefficient (γ_H) at $I = 1.0 \times 10^{-1}$ mol dm^{-3}, i.e., $\gamma_H = 0.83$ [10]. The distribution ratio (D_L) of L was calculated from the absorbance of L in the organic phase at absorption maximum before and after distribution. D_L is expressed by the following equation:

$$D_L = \frac{P_L}{1 + K_{a,HL}[H^+]}, \tag{1}$$

where P_L(=[L]$_{org}$/[L]) and $K_{a,HL}$(=[H$^+$][L]/[HL$^+$]) denote the partition coefficient of L and the acid-dissociation constant of HL$^+$, respectively. Log P_L and p$K_{a,HL}$ were determined by applying a nonlinear least-squares fitting method based on Eq. (1), being 1.30(0.04) and 3.94(0.03) for TPC and 1.38(0.05) and 4.34(0.09) for TPM, respectively, where numerical value in parenthesis denotes the standard error. The p$K_{a,HL}$ value of TPC is nearly comparable to the reported value (4.44 [4]) determined by titration method.

2.3. Measurement of distribution ratio of Hpic

An aqueous solution of $(0.00050–1.0) \times 10^{-1}$ mol dm^{-3} Hpic was shaken for 10 min with an equal volume of 1,2-dichloroethane at pH 1.48–3.16 and 25.0 ± 0.5 °C. The ionic strength (I) of the aqueous phase was adjusted to 1.0×10^{-1} mol dm^{-3} with sodium nitrate and nitric acid. The H$^+$ concentration and the distribution ratio ($D_{HX,0}$) of Hpic were determined by a manner similar to the TPC and TPM cases. $D_{HX,0}$ is expressed as follows:

$$D_{HX,0} = \frac{P_{HX}}{1 + K_{a,HX}/[H^+]}, \tag{2}$$

where P_{HX}(=[HX]$_{org}$/[HX]) and $K_{a,HX}$(=[H$^+$][X$^-$]/[HX]) denote the partition coefficient and the acid-dissociation constant of Hpic, respectively. From Eq. (2), log P_{HX} was calculated to be 2.07(0.04) by using reported p$K_{a,HX} = -0.29$ [11].

For the distribution of Hpic in the presence of TPC or TPM, an aqueous solution of $(0.50–1.0) \times 10^{-4}$ mol dm^{-3} Hpic was shaken for 10 min with an equal volume of 1,2-dichloroethane containing $(0.030–5.0) \times 10^{-1}$ mol dm^{-3} TPC or TPM at pH 2.99–5.51 and 25.0 ± 0.5 °C. The ionic strength was 1.0×10^{-1} mol dm^{-3} (H, Na)NO$_3$. After phase separation, the concentration of Hpic in both phases was determined by high performance liquid chromatography (HPLC) using octadecyl/silica-gel column. The distribution ratio (D_{HX}) of Hpic was calculated from the concentrations of Hpic in both phases.

2.4. Measurement of distribution ratio of Am(III) and Eu(III)

An aqueous solution containing both ca. 10^{-8} mol dm^{-3} ^{241}Am(III) and ^{152}Eu(III) and $(1.0–4.0) \times 10^{-2}$ mol dm^{-3} Hpic was shaken with an equal volume of organic solution containing $(1.0–20) \times 10^{-2}$ mol dm^{-3} oligo-pyridine ligand (L; TPC or TPM) for 10 min at pH 3.89–5.75 and 25.0 ± 0.5 °C. The adjustment of ionic strength (I) of the aqueous phase was kept constant at 1.0×10^{-1} mol dm^{-3} by using sodium nitrate. After phase separation, pH of the aqueous phase was measured in the same manner described above. An aliquot of each phase was taken out and the γ-activity was measured at 59.6 keV for ^{241}Am and 122 keV for ^{152}Eu with high purity Ge detector. The distribution ratio (D) of Am(III) and Eu(III) was calculated from the counting rates.

Table 1
Solvent effect on the extraction of Am(III) and Eu(III) with TPC and Hpic

Solvent	Dielectric constant [12]	pH	log *D*		SF
			Am	Eu	
Chloroform	4.806	4.73	−0.75	−1.58	6.7
1,2-Dichloroethane	10.36	4.89	0.48	−0.50	9.6
Nitrobenzene	34.82	4.87	0.60	−0.34	8.8

4.0×10^{-2} mol dm^{-3}TPC; 1.0×10^{-2} mol dm^{-3} Hpic; shaking time, 10 min; $I = 1.0 \times 10^{-1}$ mol dm^{-3} (H, Na)NO$_3$; temperature, 25 °C.

3. Results and discussion

3.1. Extraction of Am(III) and Eu(III) with L and Hpic

In order to compare effect of solvent, the extraction of Am(III) and Eu(III) with 4.0×10^{-2} mol dm^{-3} TPC and 1.0×10^{-2} mol dm^{-3} Hpic around pH 4.8 was carried out using chloroform, 1,2-dichloroethane and nitrobenzene, and these results are shown in Table 1. The *D* value increases in the order of chloroform < 1,2-dichloroethane < nitrobenzene, which is the increasing order of dielectric constant of the solvent. This suggests that the ion-pair complexes with relatively high polarity were extracted. In each solvent systems, the separation factors (SF), which is defined as SF = *D*(Am)/*D*(Eu) were 6.7–9.6, which is comparable to SF = 7 in terpyridine-2-bromodecanoic acid system [1]. This indicates that TPC has moderate affinity to Am(III) over Eu(III) as soft-donor ligand.

The plots of pH versus log *D* on the extraction of Am(III) and Eu(III) with TPC or TPM in the presence of Hpic using 1,2-dichloroethane are shown in Fig. 2. The *D* values of Am(III) and Eu(III) with TPC, TPM or Hpic alone were roughly estimated to be smaller than 10^{-4} because they were too low to calculate accurately. Therefore, the extraction of Am(III) and Eu(III) with individual reagents can be neglected. The *D* values of Am(III) and Eu(III) were highly enhanced by using a combination of TPC or TPM and Hpic and increased with a rise in pH value. Since hydrolysis of Am(III) and Eu(III) is negligible at the conditions studied [13,14], this dependency of pH is mainly due to association reaction between TPC or TPM and Hpic (described later). The *D* values of Am(III) and Eu(III) in TPM system are much lower than those in TPC system by a factor of 10^3. The SF in TPC-Hpic and TPM-Hpic systems were 8.5 and 7.4, respectively.

In the following equilibrium study, 1,2-dichloroethane was used and the extraction equilibrium of Am(III) and Eu(III) in TPC-Hpic system which gave much higher extractability of Am(III) and Eu(III) was investigated in detail.

3.2. Association equilibrium between L and HX

Since oligo-pyridine ligand and ion-pair reagent (HX) possess a basic and an acidic character, respectively, association reaction between L and Hpic is expected. To clarify the extraction with L and Hpic, it needs to study the association equilibrium of L and Hpic in order to calculate the free concentration of L and Hpic for equilibrium analysis of Am(III) and Eu(III). The association equilibrium between L and Hpic can be expressed as follows:

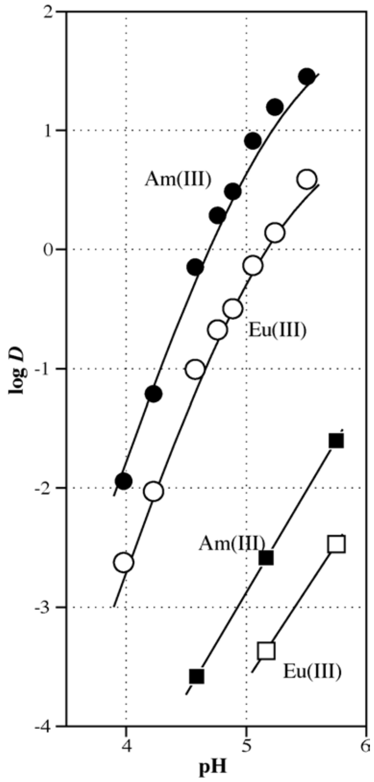

Fig. 2. Extraction of Am(III) and Eu(III) with 4.0×10^{-2} mol dm^{-3} L in the presence of 1.0×10^{-2} mol dm^{-3} Hpic in 1,2-dichloroethane. TPC-Hpic (●, ○); TPM-Hpic (■, □).

$$\mathrm{HX_{org}} + m\mathrm{L_{org}} \rightleftharpoons \mathrm{HX} \cdot m\mathrm{L_{org}}, \tag{3}$$

where the subscript, org, means the species in the organic phase. The over all association constant ($\beta_{\mathrm{ass,m}}$) is defined as,

$$\beta_{\mathrm{ass,m}} = \frac{[\mathrm{HX} \cdot m\mathrm{L}]_{\mathrm{org}}}{[\mathrm{HX}]_{\mathrm{org}}[L]^m_{\mathrm{org}}}. \tag{4}$$

The distribution ratio of Hpic in the absence and presence of L can be expressed by the following equations:

$$D_{\mathrm{HX},0} = \frac{[\mathrm{HX}]_{\mathrm{org}}}{[\mathrm{HX}] + [\mathrm{X}^-]} \tag{5}$$

and

$$D_{\mathrm{HX}} = \frac{[\mathrm{HX}]_{\mathrm{org}} + \sum[\mathrm{HX} \cdot m\mathrm{L}]_{\mathrm{org}}}{[\mathrm{HX}] + [\mathrm{X}^-]}, \tag{6}$$

respectively. The following equation is derived by dividing Eq. (6) with Eq. (5),

$$\frac{D_{\mathrm{HX}}}{D_{\mathrm{HX},0}} = 1 + \sum \beta_{\mathrm{ass,m}}[L]^m_{\mathrm{org}} \tag{7}$$

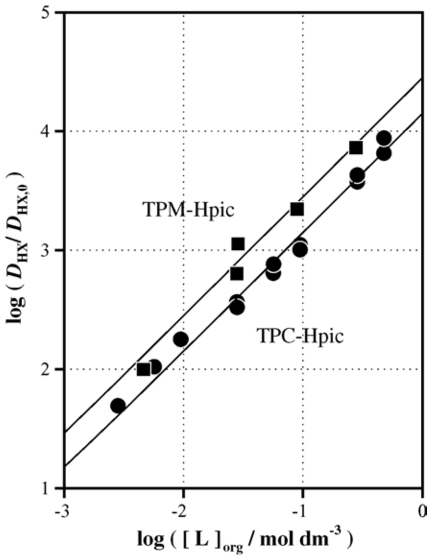

Fig. 3. Enhancement of distribution ratio of Hpic as a function of equilibrium concentration of L in the organic phase. 3.0×10^{-3}–5.0×10^{-1} mol dm^{-3} L; 5.0×10^{-5}–1.0×10^{-4} mol dm^{-3} Hpic; pH 2.99–5.51.

where $D_{HX}/D_{HX,0}$ indicates the enhancement of the distribution ratio of Hpic by the addition of L. In 1,2-dichloroethane system, the logarithmic plots of $D_{HX}/D_{HX,0}$ versus $[L]_{org}$ in Eq. (7) is shown in Fig. 3. The equilibrium concentration of L, $[L]_{org}$, was calculated from $[L]_{org} = C_L P_L K_{a,HL}/([H^+] + K_{a,HL} + K_{a,HL} P_L)$, where C_L denotes total concentration of L. Since the plots in both TPC-Hpic and TPM-Hpic system give a straight line with a slope of unity in the wide concentration range of L, it is found that an association complex of Hpic·L predominantly forms in the organic phase. The corresponding $\log \beta_{ass,1}$ values in TPC-Hpic and TPM-Hpic systems were determined by Eq. (7) to be 4.15(0.02) and 4.42(0.04), respectively.

3.3. Equilibrium analysis on the extraction of Am(III) and Eu(III) with TPC and Hpic

In order to check shaking time to attain extraction equilibrium, the extraction of Am(III) and Eu(III) with 1.0×10^{-2} mol dm^{-3} TPC and 1.0×10^{-2} mol dm^{-3} Hpic in 1,2-dichloroethane was carried out at pH 5.30–5.31. The logarithmic values of D for Am(III) and Eu(III) during 10–60 min gave constant values, i.e., 1.34 and 0.26, respectively, which is independent of the shaking time.

It was reported that TPC forms binuclear metal lanthanide complex [7]. In addition, if there is polymerization or dissociation of the extracted species in the organic phase, the D of Am(III) and Eu(III) should be dependent on the metal concentration. To ascertain this, the extraction of Am(III) and Eu(III) with 1.0×10^{-2} mol dm^{-3} TPC and 1.0×10^{-2} mol dm^{-3} Hpic was carried out in the presence of 1.0×10^{-7}–1.0×10^{-4} mol dm^{-3} Eu(III) carrier. The Eu(III) solution labeled with ^{152}Eu(III) was prepared from ^{152}Eu(III) and $Eu(NO_3)_3$ solutions in the same manner as carrier-free ^{152}Eu(III) solution. The $\log D$ values of Am(III) and Eu(III) were −0.42 and −1.34, respectively, at pH 5.19–5.20, which are irrespective of the total concentration of Eu(III). Therefore, it was confirmed that the extracted species are monomer and are undissociated in the organic phase.

Since the extraction of Am(III) and Eu(III) with L alone from 1.0×10^{-1} mol dm^{-3} nitrate solution into 1,2-dichloroethane is negligible as described above, only pic$^-$ acts as a counter anion to electronically neutralize trivalent metal ion (M^{3+}) on the extraction with L and Hpic. Therefore, the extraction equilibrium can be simply assumed as follows:

$$M^{3+} + xL + 3X^- \rightleftharpoons ML_xX_{3,org}, \tag{8}$$

$$K_{ex} = \frac{[ML_xX_3]_{org}}{[M^{3+}][L]^x[X^-]^3}, \tag{9}$$

where K_{ex} denotes the extraction constant of M^{3+}. The following equation is derived by inserting $D = [ML_xX_3]/[M^{3+}]$ into Eq. (9),

$$D = K_{ex}[L]^x[X^-]^3. \tag{10}$$

The D value is dependent on the equilibrium concentration of L and pic$^-$ as shown in Eq. (10).

Since the association between TPC and Hpic occurs in the organic phase as mentioned above, the equilibrium concentration of free L and pic$^-$ must be calculated using the $\beta_{ass,1}$. The following simultaneous equations are derived on the basis of the mass balance of each reagent,

$$\begin{aligned} C_L = (1 + P_L + [H^+]K_{a,HL}^{-1} \\ + \beta_{ass,1} P_L P_{HX} [H^+][X^-] K_{a,HX}^{-1})[L], \end{aligned} \tag{11}$$

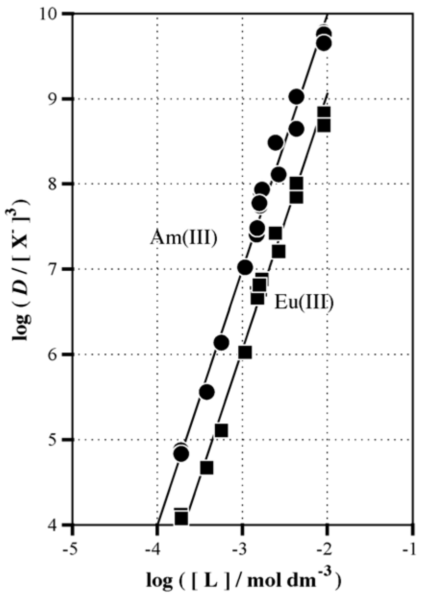

Fig. 4. Dependence of the distribution ratio of Am(III) and Eu(III) as a function of equilibrium concentration of TPC in the aqueous phase in TPC-Hpic-1,2-dichloroethane system. 1.0×10^{-2}–2.0×10^{-1} mol dm^{-3} TPC; (1.0–4.0) $\times 10^{-2}$ mol dm^{-3} Hpic; pH 3.89–5.44.

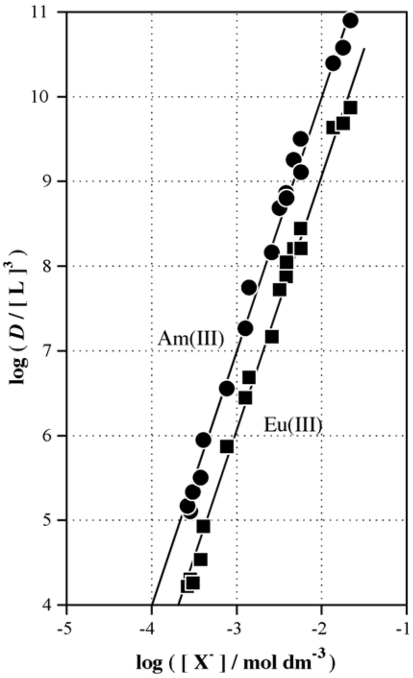

Fig. 5. Dependence of the distribution ratio of Am(III) and Eu(III) as a function of equilibrium concentration of pic$^-$ in the aqueous phase in TPC-Hpic-1,2-dichloroethane system. 1.0×10^{-2}–2.0×10^{-1} mol dm^{-3} TPC; (1.0–4.0) $\times 10^{-2}$ mol dm^{-3} Hpic; pH 3.89–5.44.

$$C_{\mathrm{HX}} = (1 + P_{\mathrm{HX}} + [\mathrm{H}^+]K_{\mathrm{a,HX}}^{-1} + P_{\mathrm{HX}}[\mathrm{H}^+]K_{\mathrm{a,HX}}^{-1} + \beta_{\mathrm{ass},1} P_{\mathrm{L}} P_{\mathrm{HX}}[\mathrm{H}^+][\mathrm{L}]K_{\mathrm{a,HX}}^{-1})[\mathrm{X}^-], \quad (12)$$

where C_{L} and C_{HX} stand for the total concentration of L and Hpic, respectively. The equilibrium concentrations of L and pic$^-$ in the aqueous phase were calculated from Eqs. (11) and (12).

Fig. 4 shows the logarithmic plots of $D[\mathrm{pic}^-]^{-3}$ versus [TPC] based on transposed Eq. (10), $D[\mathrm{X}^-]^{-3} = K_{\mathrm{ex}}[\mathrm{L}]^x$. The plots of Am(III) and Eu(III) give a straight line with a slope of 3.0. This suggests that TPC predominantly forms the 1:3 complex with Am(III) and Eu(III) in the presence of Hpic. To confirm the composition of pic$^-$ in the extracted species, the logarithmic plots of $D[\mathrm{TPC}]^{-3}$ versus [pic$^-$] based on $D[\mathrm{L}]^{-3} = K_{\mathrm{ex}}[\mathrm{X}^-]^y$ were analyzed in terms of the slope of Am(III) and Eu(III) (Fig. 5). These plots of Am(III) and Eu(III) give a straight line with a slope of 3.0, which is quite consistent with ionic charge of the metal ions.

The both TPC-Hpic and TPM-Hpic systems show similar distribution equilibrium of the reagents. The magnitudes of $\beta_{\mathrm{ass},1}$, P_{L} and $K_{\mathrm{a,HL}}$ in TPM-Hpic system were comparable to those in TPC-Hpic as well. TPC-Hpic system, however, gave much larger distribution ratio of Am(III) and Eu(III) than TPM system on the extraction as shown in Fig. 2. Assuming that the extraction equilibrium of Am(III) and Eu(III) in TPM system is similar to those in TPC system, this result might be ascribed to low stability of $\mathrm{M(TPM)_3(pic)_3}$, which might be owing to steric effect of the methoxy group of TPM on the conformation of donating pyridyl groups with the metal ions.

On the basis of the results of the equilibrium analysis, in TPC-Hpic system, it was found that the predominant species of Am(III) and Eu(III) extracted into 1,2-dichloroethane are ion-pair complex, $\mathrm{M(TPC)_3(pic)_3}$, and that Am(III) and Eu(III) are coordinated to not oxygen atom on the alkoxy group of TPC but nitrogen atoms on the pyridyl groups. These results show that the binuclear metal complexes [7] as reported does not form on the solvent extraction with TPC and Hpic. The binuclear complex formation must be dependent on the solvent used. The log K_{ex} values were determined by using Eq. (10) to be 15.99(0.04) for Am(III) and 15.06(0.04) for Eu(III) from the plots in Figs. 4 and 5. TPC-Hpic system extracts Am(III) more effectively than Eu(III). The separation factor of Am(III) over Eu(III) was estimated to be 8.5 from K_{ex} values.

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