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Effect of the Hydrophobic Anion of Picrate on the Extraction of Europium(III) with Diamide

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The effect of the picrate (pic^-) ion on Eu(III) extraction with a diamide (**da**) from aqueous nitric acid (0.001—0.1 mol dm^{-3}) solutions into benzene was clarified on the basis of the stoichiometry of ion-pair extractions by analyzing the distribution data of Eu(III) and picric acid (Hpic). The extraction of Eu(III) with **da** was extremely enhanced by adding a hydrophobic anion of pic^- to the liquid–liquid system. From analyses of the distribution data of Eu(III) and Hpic, it was concluded that the effect of the hydrophobic anion was caused by the extraction of a single ion-pair of $[\text{Eu}(\textbf{da})_2](\text{pic})_3$. The nitrate ion had no relation with the cooperative effect of **da** and pic^-, i.e., the extraction of $[\text{Eu}(\textbf{da})_2](\text{NO}_3)_3$, $[\text{Eu}(\textbf{da})_2](\text{pic})(\text{NO}_3)_2$, and $[\text{Eu}(\textbf{da})_2](\text{pic})_2(\text{NO}_3)$ was practically negligible as against the $[\text{Eu}(\textbf{da})_2](\text{pic})_3$ extraction. The cooperative effect was reduced by an increase in the aqueous HNO_3 concentration, which was induced by a decrease in the pic^- concentration in the aqueous phase; the dissociation of Hpic into pic^- ion was suppressed by an increase in the H^+ concentration, and a part of molecular Hpic was extracted into the organic phase. Furthermore, the extraction of Hpic was also enhanced by an increase in the **da** concentration in the organic phase, which also induced a decrease in the aqueous pic^- concentration. This was found to be due to the formation of a 1 : 1 complex between **da** and Hpic. However, the extraction of the complexes between **da** and HNO_3 was negligible in the acid concentration range in the present study.

In our laboratory, new extractants that are potentially useful for a separation process of both actinides and lanthanides from aqueous nitric acid solutions in the nuclear-fuel cycle are being studied. A diamide, which can work as a bidentate extractant, is one of the most hopeful new extractants for this purpose, especially from the viewpoint of its perfect combustibility and nontoxicity.[1—10] However, the extractability of diamide is generally not very high. In order to improve the extractability, the cooperative effect of a diamide and a hydrophobic anion on the extraction of europium(III) was examined in the present study. The picrate ion, which is well-known as a bulky and hydrophobic anion, was chosen as such. Picrate ions work very effectively, indeed, on the europium(III) extraction with the diamide as counter-ions for a europium(III)–diamide complex cation, which is similar to the ion-pair extraction with a stable and bulky cobalt(III) dicarbollide anion developed as a novel extractant.[11] The mechanism of the anion effect has been clarified by analyzing the data of the distribution of europium(III) and picric acid between aqueous nitric acid solution and benzene.

Experimental

All of the chemicals were of reagent grade. A bulky diamide (**da**), *N*,*N*′-dioctyl-*N*,*N*′-dimethyl-2-(3-oxapentadecyl)propane-1,3-diamide, which was originally synthesized by Wako Pure Chemical Industries Ltd., Japan, was used in the experiments; the purity, determined by liquid chromatography, was 99.4%. Nitric acid and picric acid (Hpic) in aqueous solutions were standardized by titration and spectrophotometry, respectively. The experiments in the present study were carried out at 298 K. The experimental procedure was as follows. An aqueous nitric acid (0.001—0.1 mol dm^{-3}) solution containing 6.6×10^{-6} mol dm^{-3} (1 ppm) Eu(III) and Hpic (0.001—0.01 mol dm^{-3}) and the same volume of a benzene solution containing **da** (0.01—0.1 mol dm^{-3}) were placed in a stoppered glass tube; for experiments at a high Hpic concentration (0.1 mol dm^{-3}), Hpic was dissolved in benzene, since the solubility of Hpic in benzene is much larger than that in water. The two phases were vigorously agitated for 15 min, and then centrifuged. The concentration of Eu(III) in the aqueous phase and that in the organic phase after being stripped into an aqueous oxalic acid solution were measured by means of an ICP-mass spectrometer (Fisons, PQΩ). The concentration of Hpic and that of HNO_3 in both phases were also measured. These acids in the organic phase were back-extracted into an aqueous sodium hydroxide solution. The concentration of picrate (pic^-) was determined by means of a UV-visible spectrophotometer (Shimadzu, UV2200); ε = 13400 at λ = 380 nm in water. The concentration of NO_3^- was determined by ion chromatography using an aqueous potassium hydrogen phthalate solution; the details were given in a previous paper.[12] The concentration of **da** in the aqueous phase was also checked by liquid chromatography using a methanol–water eluent.

Theoretical

Extraction of Eu(III) by Only Diamide. When picric acid (Hpic) is absent in the liquid–liquid system, the Eu(III) ion, coordinated with the diamide (**da**) molecules, can be extracted together with NO_3^- ions; since the valence of europium is 3+, three NO_3^- ions are accompanied by a Eu(III)–**da** complex cation. Hence, the equilibrium for the

Eu(III) extraction with **da** from an aqueous HNO_3 solution can be written as:

$$Eu^{3+} + x\,\mathbf{da}_{(org)} + 3NO_3^- \rightleftarrows [Eu(\mathbf{da})_x](NO_3)_{3(org)} \quad (x = 1,2,3,\cdots)$$

$$K_{ex,\mathbf{da}} = \frac{[[Eu(\mathbf{da})_x](NO_3)_3]_{org}}{\{Eu^{3+}\}[\mathbf{da}]_{org}^x\{NO_3^-\}^3}, \tag{1}$$

where the subscript "org" denotes the species in the organic phase, while the lack of a subscript denotes those in the aqueous phase. The activity of ions in the aqueous phase is expressed by { }. For electrically neutral species, i.e., molecules and ion-pairs, in both aqueous and organic phases, an activity correction is not made. Because it is not very important, since there is no effect of the ionic atmosphere by the Coulomb force on such neutral species,[13] details of the question will be considered in Results and Discussion. When aqueous HNO_3 concentration is not higher than 0.1 mol dm^{-3}, the hydration terms do not have to be taken into account, because the water activity (a_w) is approximately constant at one; $a_w^{aq}(= a_w^{org}) = 0.9979^{14} \approx 1$ when the total aqueous nitric acid concentration ($[HNO_3]_t$) is not higher than 0.1 mol dm^{-3}. Thus, hydration of the species in the liquid–liquid system is not expressed in the equilibria in the present study. The distribution ratio of Eu(III) can be written as:

$$D_{Eu} = \frac{[Eu(NO_3)_3]_{org} + \sum_{x=1}[[Eu(\mathbf{da})_x](NO_3)_3]_{org}}{\{Eu^{3+}\}} \approx \sum_{x=1} K_{ex,\mathbf{da}}[\mathbf{da}]_{org}^x\{NO_3^-\}^3, \tag{2}$$

where the extraction of $Eu(NO_3)_3$ into benzene is negligible as against that of $[Eu(\mathbf{da})_x](NO_3)_3$. From this equation, the distribution ratio of Eu(III) is in proportion to $\{NO_3^-\}$ raised to the third power, when $[\mathbf{da}]_{org}$ is constant. On the other hand, when $\{NO_3^-\}$ is constant, the distribution ratio of Eu(III) is in proportion to $[\mathbf{da}]_{org}$ raised to the power of the binding number of **da**, x. The Eu(III) distribution data can be analyzed by means of Eq. 2 to determine the number of x and the overall extraction equilibrium constant.

Extraction of Eu(III) by Only Picrate Ion. When the diamide (**da**) is not added to the liquid–liquid system, Eu(III) can be extracted as its picrate into benzene. Hence, three pic$^-$ ions are accompanied with a Eu(III) ion:

$$Eu^{3+} + 3\,pic^- \rightleftarrows Eu(pic)_{3(org)}$$

$$K_{ex,Hpic} = \frac{[Eu(pic)_3]_{org}}{\{Eu^{3+}\}\{pic^-\}^3}. \tag{3}$$

The distribution ratio of Eu(III) can be written as:

$$D_{Eu} = \frac{[Eu(NO_3)_3]_{org} + [Eu(pic)_3]_{org}}{\{Eu^{3+}\}} \approx K_{ex,Hpic}\{pic^-\}^3, \tag{4}$$

where the extraction of $Eu(NO_3)_3$ into benzene is negligible as against that of $Eu(pic)_3$. From this equation, the distribution ratio of Eu(III) is in proportion to $\{pic^-\}$ raised to the third power.

Cooperative Extraction of Eu(III) by Diamide and Picrate Ion. The effect of the hydrophobic anion of pic$^-$ can be caused by the following ion-pair extractions:

$$Eu^{3+} + p\,\mathbf{da}_{(org)} + q\,pic^- + r\,NO_3^- \rightleftarrows [Eu(\mathbf{da})_p](pic)_q(NO_3)_{r(org)} \quad (p = 1,2,3,\cdots,\ q = 1,2,3,\ r = 0,1,2)$$

$$K_{ex,\mathbf{da}\text{-}Hpic} = \frac{[[Eu(\mathbf{da})_p](pic)_q(NO_3)_r]_{org}}{\{Eu^{3+}\}[\mathbf{da}]_{org}^p\{pic^-\}^q\{NO_3^-\}^r}. \tag{5}$$

The distribution ratio of Eu(III) can be written as:

$$\begin{aligned} D_{Eu} &\approx \frac{[Eu(pic)_3]_{org} + \sum_{x=1}[[Eu(\mathbf{da})_x](NO_3)_3]_{org}}{\{Eu^{3+}\}} + \frac{\sum_{p=1}\sum_{q=1}\sum_{r=0}[[Eu(\mathbf{da})_p](pic)_q(NO_3)_r]_{org}}{\{Eu^{3+}\}} \\ &= K_{ex,Hpic}\{pic^-\}^3 + \sum_{x=1} K_{ex,\mathbf{da}}[\mathbf{da}]_{org}^x\{NO_3^-\}^3 \\ &\quad + \sum_{p=1}\sum_{q=1}\sum_{r=0}(K_{ex,\mathbf{da}\text{-}Hpic}[\mathbf{da}]_{org}^p\{pic^-\}^q\{NO_3^-\}^r), \end{aligned} \tag{6}$$

where the extraction of $Eu(NO_3)_3$ is negligible.

Distribution of Picric Acid. The dissociation of Hpic into pic$^-$ is suppressed by an increase in the H^+ concentration, and a part of molecular Hpic is extracted into benzene.

$$Hpic \rightleftarrows Hpic_{(org)}$$

$$K_{d,Hpic} = \frac{[Hpic]_{org}}{[Hpic]}. \tag{7}$$

When the diamide (**da**) is absent, the distribution ratio of Hpic can be written as:

$$D_{Hpic} = \frac{[Hpic]_{org}}{\{pic^-\} + [Hpic]} = \frac{K_{d,Hpic}\{H^+\}}{K_a + \{H^+\}}. \tag{8}$$

From this,

$$D_{Hpic}(K_a + \{H^+\}) = K_{d,Hpic}\{H^+\}, \tag{9}$$

where $\{H^+\}$ ($= \gamma_{H^+}[H^+]$) is the activity of H^+, and K_a ($= \{H^+\}\{pic^-\}/[Hpic]$) is the dissociation constant of Hpic in the aqueous phase; γ_{H^+} is the activity coefficient, and $[H^+]$ can be obtained by the relationship $[H^+] = [NO_3^-] + [pic^-]$ (charge balance in the aqueous phase). The distribution constant of Hpic, $K_{d,Hpic}$, can be obtained by using this equation.

Complex Formation between Diamide and Picric Acid. The complex formation equilibrium between the diamide (**da**) and Hpic in the organic phase can be written as:

$$m\,\mathbf{da}_{(org)} + n\,Hpic_{(org)} \rightleftarrows (\mathbf{da})_m(Hpic)_{n(org)} \quad (m = 1,2,3,\cdots, n = 1,2,3,\cdots)$$

$$K_{com,\mathbf{da}\text{-}Hpic} = \frac{[(\mathbf{da})_m(Hpic)_n]_{org}}{[\mathbf{da}]_{org}^m[Hpic]_{org}^n}. \tag{10}$$

Thus, the distribution ratio of Hpic can be written as:

$$D_{Hpic} = \frac{[Hpic]_{org} + \sum_{m=1}\sum_{n=1} n[(\mathbf{da})_m(Hpic)_n]_{org}}{\{pic^-\} + [Hpic]}$$

$$= K_{\mathrm{d,Hpic}}\{\mathrm{H}^+\} \times \frac{[1+\sum_{m=1}\sum_{n=1} n\, K_{\mathrm{com,}\mathbf{da}\text{-}\mathrm{Hpic}}(K_{\mathrm{d,Hpic}}\{\mathrm{H}^+\}\{\mathrm{pic}^-\})^{n-1}[\mathbf{da}]_{\mathrm{org}}{}^{m}]}{K_\mathrm{a}+\{\mathrm{H}^+\}} . \quad (11)$$

From this, the following equation can be obtained:

$$D_{\mathrm{Hpic}}(K_\mathrm{a}+\{\mathrm{H}^+\})/(K_{\mathrm{d,Hpic}}\{\mathrm{H}^+\})-1 = \sum_{m=1}\sum_{n=1} n\, K_{\mathrm{com,}\mathbf{da}\text{-}\mathrm{Hpic}}(K_{\mathrm{d,Hpic}}\{\mathrm{H}^+\}\{\mathrm{pic}^-\})^{n-1}[\mathbf{da}]_{\mathrm{org}}{}^{m} . \quad (12)$$

Results and Discussion

Cooperative Effect of Diamide and Picric Acid on Eu(III) Extraction. Figure 1 gives the distribution ratio of Eu(III) as a function of the aqueous HNO_3 concentration at various picric acid (Hpic) concentrations. The picric acid was added to the liquid–liquid system in the initial concentration, $[\mathrm{Hpic}]_{\mathrm{init}}$, from 0.001 to 0.01 mol dm^{-3}, while the total concentration of the diamide (**da**) in the organic phase, $[\mathbf{da}]_{\mathrm{org,t}}$, was fixed at 0.1 mol dm^{-3}. The circle key in this figure indicates the experimental data of the cooperative Eu(III) extraction by **da** (0.1 mol dm^{-3}) and Hpic (0.001—0.01 mol dm^{-3}), and the triangle key indicates the experimental Eu(III) extraction with only 0.1 mol dm^{-3}**da**. The solid and dotted lines indicate the calculated values by using the equilibrium constants, $K_{\mathrm{ex,}\mathbf{da}\text{-}\mathrm{Hpic}}$ and $K_{\mathrm{ex,}\mathbf{da}}$, in Table 1, respectively; the process of determining these values is shown below. The chain line indicates the calculated Eu(III) extraction with only 0.01 mol dm^{-3}Hpic; since to obtain the data in such a low distribution range is difficult, only a line calculated by using the extraction equilibrium constant of Eu(III) picrate, $K_{\mathrm{ex,Hpic}}$, that was obtained at high Hpic concentration (0.1 mol dm^{-3}), is indicated. As can be seen from Fig. 1, the extraction of Eu(III) with **da** was greatly enhanced by the addition of Hpic; however, the extraction of Eu(III) with only **da** or Hpic was quite small.

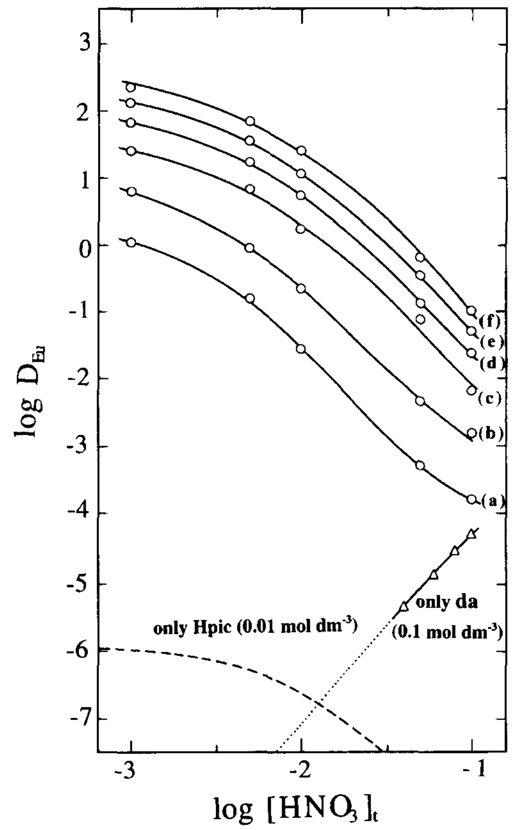

Fig. 1. Distribution ratio of Eu(III) as a function of $[HNO_3]_t$ at various picric acid concentration initially added to the system ($[\mathrm{Hpic}]_{\mathrm{init}}$) when $[\mathbf{da}]_{\mathrm{org,t}}$ is fixed at 0.1 mol dm^{-3}: $[\mathrm{Hpic}]_{\mathrm{init}}$ = (a) 0.001, (b) 0.002, (c) 0.004, (d) 0.006, (e) 0.008, and (f) 0.010 mol dm^{-3}. The solid lines indicate calculated values by using the equilibrium constants in Tables 1 and 2.
○ : 0.1 mol dm^{-3} **da** + 0.001—0.010 mol dm^{-3} Hpic,
△ : only 0.1 mol dm^{-3} **da**,
···· : only 0.1 mol dm^{-3} **da** (calculated values),
- - - : only 0.01 mol dm^{-3} Hpic (calculated values).

Extraction of Eu(III) by Only Diamide. Figure 2 shows the distribution ratio of Eu(III) with a sole extractant of **da**, whose concentration was fixed at 0.1 mol dm^{-3}, as a function of NO_3^- activity, $\{NO_3^-\}$. The activities of the NO_3^- ion were calculated by using the Debye–Hückel theoretical equation; 3 Å was employed as an ion size parameter for NO_3^- in this equation.[15] From this figure, the number of NO_3^- ions, extracted with a Eu(III)–**da** complex cation, was

Table 1. Extraction Equilibrium Constants of Eu(III) Obtained by Analyzing Eu(III) Distribution Data
3σ error for each constant is also shown.

Extracted species	Equilibrium constant
$[\mathrm{Eu}(\mathbf{da})_2](\mathrm{pic})_3$	$K_{\mathrm{ex,}\mathbf{da}\text{-}\mathrm{Hpic}} = 7.10 \times 10^{11}$ $(\pm 5 \times 10^{9})$
$[\mathrm{Eu}(\mathbf{da})_2](\mathrm{NO}_3)_3$	$K_{\mathrm{ex,}\mathbf{da}} = 1.17 \times 10^{1}$ $(\pm 5 \times 10^{-1})$
$\mathrm{Eu}(\mathrm{pic})_3$	$K_{\mathrm{ex,Hpic}} = 1.25 \times 10^{1}$ $(\pm 5 \times 10^{-1})$

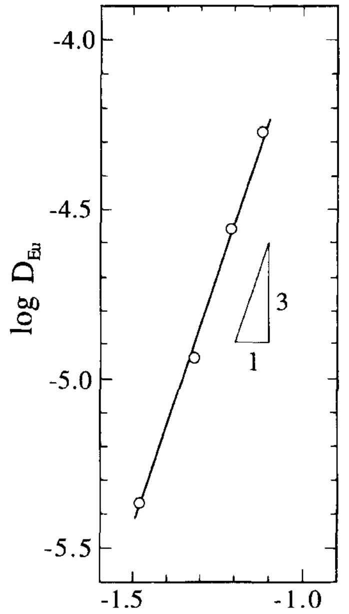

Fig. 2. Distribution ratio of Eu(III) as a function of $\{NO_3^-\}$ at a fixed $[\mathbf{da}]_{\mathrm{org,t}}$ to be 0.1 mol dm^{-3}.

found to be three, as is evident from Eq. 2.

Figure 3 gives the distribution ratio of Eu(III) as a function of the **da** concentration at $[\mathrm{HNO_3}]_t = 0.1\ \mathrm{mol\,dm^{-3}}$. From the slope of the plot in this figure, the binding number of **da** to a Eu(III) ion, x, was found to be two. From analyses of the data in Figs. 2 and 3, the value of $K_{\mathrm{ex,da}}$ for the extraction of $[\mathrm{Eu(\mathbf{da})_2}](\mathrm{NO_3})_3$ was obtained as shown in Table 1.

Extraction of Eu(III) by Only Picric Acid. Figure 4 gives the Eu(III) extraction from aqueous $\mathrm{HNO_3}$ solutions (0.01—0.1 $\mathrm{mol\,dm^{-3}}$) with only Hpic (0.1 $\mathrm{mol\,dm^{-3}}$ added as initial concentration) as a function of the $\mathrm{pic^-}$ activity in the aqueous phase, $\{\mathrm{pic^-}\}$; since the dissociation of Hpic into $\mathrm{pic^-}$ is suppressed by an increase in the $\mathrm{H^+}$ concentration, and a part of molecular Hpic is distributed to the organic phase, the change in the aqueous $\mathrm{HNO_3}$ concentration produces a variation of $\{\mathrm{pic^-}\}$. The concentration of $\mathrm{pic^-}$ in the aqueous phase, $[\mathrm{pic^-}]$, was directly determined by measuring the $\mathrm{pic^-}$ absorbance at 380 nm; molecular Hpic has no absorption at this wavelength. An activity correction for the $\mathrm{pic^-}$ ion was also made by using the Debye–Hückel theoretical equation; 7 Å was used as an ion size parameter for $\mathrm{pic^-}$ ion in this equation.[15] From Fig. 4, the number of $\mathrm{pic^-}$ ions extracted with a Eu(III) ion was found to be three, as is evident from Eq. 3. The value of $K_{\mathrm{ex,Hpic}}$ was also obtained as shown in Table 1.

Stoichiometry of the Cooperative Extraction by Diamide and Picrate Ion. Figure 5 shows the decrease in $\{\mathrm{pic^-}\}$ by an increase in $[\mathrm{HNO_3}]_t$ from 0.001 to 0.1 $\mathrm{mol\,dm^{-3}}$ at $[\mathbf{da}]_{\mathrm{org},t} = 0.1\ \mathrm{mol\,dm^{-3}}$, which is given as a function of $[\mathrm{Hpic}]_{\mathrm{init}}$; $\{\mathrm{pic^-}\}$ was determined for the same samples as those in Fig. 1. From Fig. 5, $\{\mathrm{pic^-}\}$ seems to be very much dependent not only on $[\mathrm{Hpic}]_{\mathrm{init}}$ but also on $[\mathrm{HNO_3}]_t$; this should be the reason why the cooperative effect of **da** and Hpic is reduced by an increase in the aqueous $\mathrm{HNO_3}$ concentration, as can be seen in Fig. 1. The distribution ratio of Eu(III) plotted against $\{\mathrm{pic^-}\}$ in Fig. 6 shows a single straight line having a slope of three, which is independent of $[\mathrm{HNO_3}]_t$; the keys in this figure, which indicate the respective $[\mathrm{HNO_3}]_t$, are the same as those in Fig. 5. From

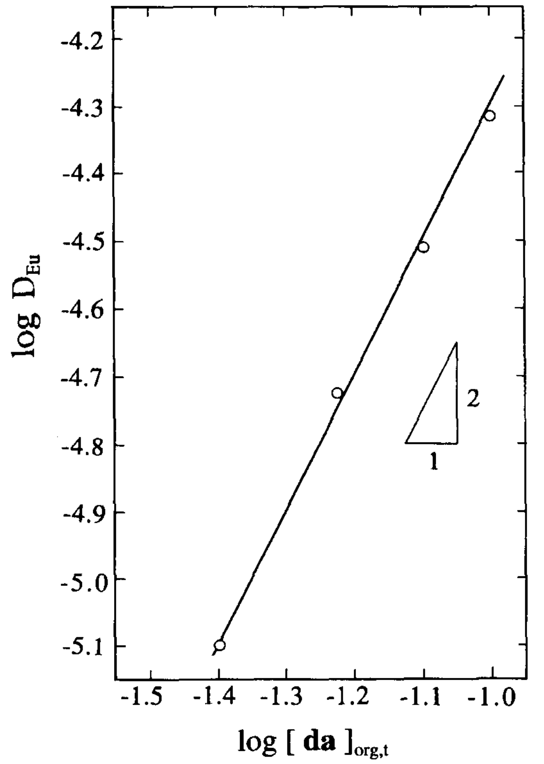

Fig. 3. Distribution ratio of Eu(III) as a function of $[\mathbf{da}]_{\mathrm{org},t}$ at a fixed $[\mathrm{HNO_3}]_t$ to be 0.1 $\mathrm{mol\,dm^{-3}}$.

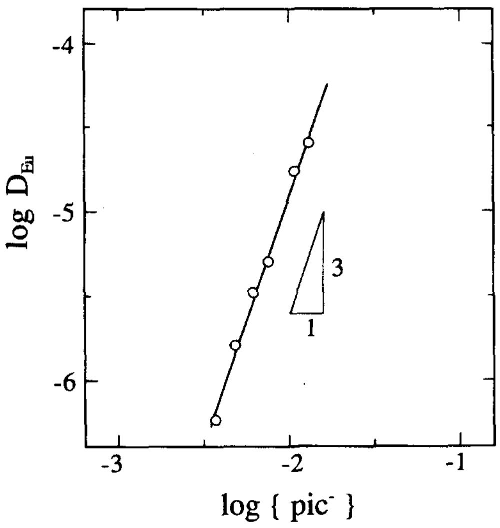

Fig. 4. Distribution ratio of Eu(III) as a function of $\{\mathrm{pic^-}\}$; $[\mathrm{Hpic}]_{\mathrm{init}}$ is fixed at 0.1 $\mathrm{mol\,dm^{-3}}$, while $[\mathrm{HNO_3}]_t$ is varied from 0.01 to 0.1 $\mathrm{mol\,dm^{-3}}$.

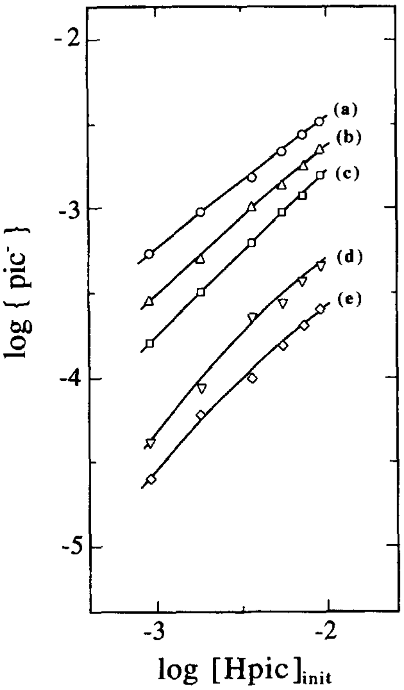

Fig. 5. Activity of $\mathrm{pic^-}$ in the aqueous phase as a function of $[\mathrm{Hpic}]_{\mathrm{init}}$ at various $[\mathrm{HNO_3}]_t$ when $[\mathbf{da}]_{\mathrm{org},t}$ is fixed at 0.1 $\mathrm{mol\,dm^{-3}}$; $[\mathrm{HNO_3}]_t$ = (a) 0.001, (b) 0.005, (c) 0.01, (d) 0.05, (e) 0.1 $\mathrm{mol\,dm^{-3}}$. The solid lines indicate calculated values by using the equilibrium constants in Table 2.

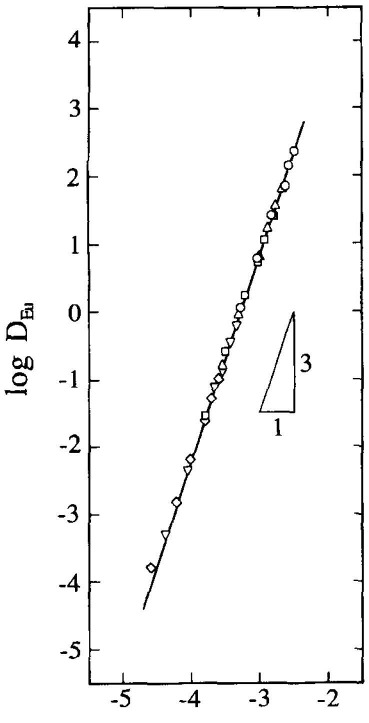

Fig. 6. Distribution ratio of Eu(III) as a function of $\{\mathrm{pic}^-\}$ at a fixed $[\mathbf{da}]_{\mathrm{org,t}}$ to be 0.1 mol dm^{-3}; $[\mathrm{Hpic}]_{\mathrm{init}}$ = 0.001—0.01 mol dm^{-3}, $[\mathrm{HNO_3}]_{\mathrm{t}}$ = ○ 0.001, △ 0.005, □ 0.01, ▽ 0.05 ◇ 0.1 mol dm^{-3}, respectively.

this result, it is concluded that the cooperative effect is caused by only the extraction of the ion-pairs including three pic$^-$ ions ($q = 3$). In other words, the extraction of the ion-pairs including $\mathrm{NO_3}^-$ ions is quite negligible as against that of $[\mathrm{Eu}(\mathbf{da})_p](\mathrm{pic})_3$ ($p = 1,2,3,\cdots$), i.e., $r = 0$ in Eqs. 5 and 6.

The Eu(III) distribution ratio as a function of the diamide (**da**) concentration was also measured at various aqueous $\mathrm{HNO_3}$ concentrations (0.005, 0.05, and 0.1 mol dm^{-3}) at a fixed $[\mathrm{Hpic}]_{\mathrm{init}}$ (0.01 mol dm^{-3}). By plotting the distribution ratio of Eu(III) divided by the third power of $\{\mathrm{pic}^-\}$ against $[\mathbf{da}]_{\mathrm{org,t}}$, only a single straight line having a slope of two was obtained, as is shown in Fig. 7. Thus, the binding number of **da** to a Eu(III) ion, p in $[\mathrm{Eu}(\mathbf{da})_p](\mathrm{pic})_3$, was found to be two, which was independent of the $\mathrm{HNO_3}$ concentration. Finally, it is concluded that the extraction of only a single ion-pair, $[\mathrm{Eu}(\mathbf{da})_2](\mathrm{pic})_3$, governs the cooperative effect. The binding number of **da** to a Eu(III) ion was the same; nevertheless, the counter ion was different, i.e., $x = p = 2$. The cooperative extraction equilibrium constant of Eu(III), $K_{\mathrm{ex,da\text{-}Hpic}}$, which corresponds to the extraction equilibrium constant of $[\mathrm{Eu}(\mathbf{da})_2](\mathrm{pic})_3$, is given in Table 1.

Distribution of Picric Acid. As mentioned before, the cooperative effect is reduced by an increase in the aqueous $\mathrm{HNO_3}$ concentration, which is caused by a decrease in the pic$^-$ ion concentration in the aqueous phase. Figure 8 gives $D_{\mathrm{Hpic}}(K_{\mathrm{a}} + \{\mathrm{H}^+\})$ as a function of $\{\mathrm{H}^+\}$, where D_{Hpic} is the distribution ratio of Hpic between an aqueous $\mathrm{HNO_3}$ solution and benzene containing no diamide (**da**). The activities of the H^+ ion were also calculated by the Debye–Hückel theoretical equation; 9 Å was used as an ion size parameter for the H^+ ion in this equation.[15] On the basis of Eq. 9, the value of the distribution constant of Hpic, $K_{\mathrm{d,Hpic}}$, was obtained from the intercept of a straight line having a slope of one, which implies no polymerization of Hpic in the organic phase; $K_{\mathrm{a}} = 10^{-0.29}$ (at 25 °C), which was taken from the literature,[16] was introduced into this equation. The thus-obtained $K_{\mathrm{d,Hpic}}$ value is given in Table 2.

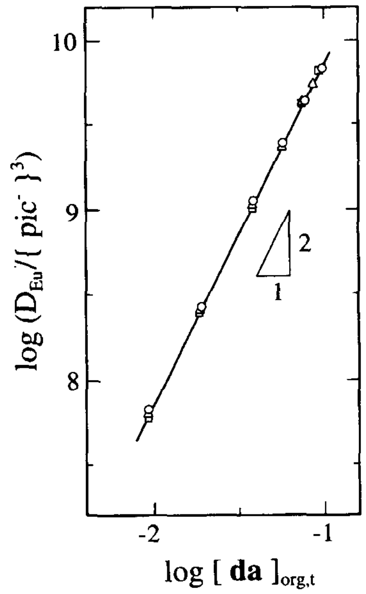

Fig. 7. Distribution ratio of Eu(III) divided by the third power of $\{\mathrm{pic}^-\}$ as a function of $[\mathbf{da}]_{\mathrm{org,t}}$ at various $[\mathrm{HNO_3}]_{\mathrm{t}}$ when $[\mathrm{Hpic}]_{\mathrm{init}}$ is fixed at 0.01 mol dm^{-3}; $[\mathrm{HNO_3}]_{\mathrm{t}}$ = ○ 0.005, △ 0.05, □ 0.1 mol dm^{-3}.

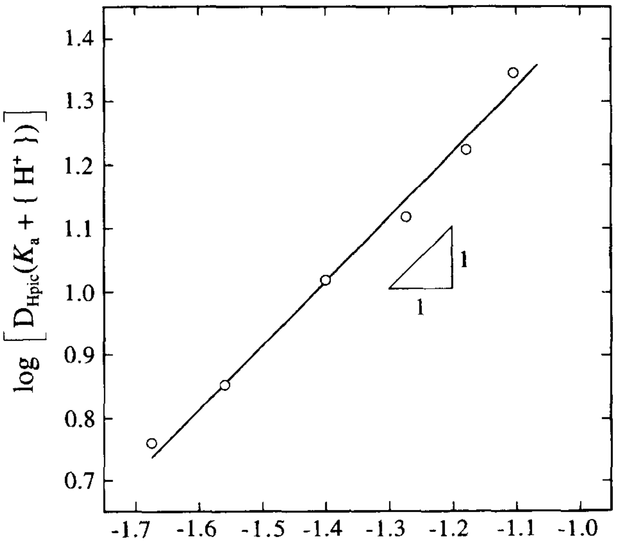

Fig. 8. $D_{\mathrm{Hpic}}(K_{\mathrm{a}}+\{\mathrm{H}^+\})$ as a function of $\{\mathrm{H}^+\}$ when **da** is absent; $[\mathrm{Hpic}]_{\mathrm{init}} = 0.1$ mol dm^{-3} = const, $[\mathrm{HNO_3}]_{\mathrm{t}} = 0.01$— 0.1 mol dm^{-3}.

Complex Formation between Diamide and Picric Acid. The extraction of Hpic into the organic phase is also increased

Table 2. Distribution Equilibrium Constant of Hpic and the Equilibrium Constant of Complexation between **da** and Hpic in the Organic Phase Obtained by Analyzing Hpic Distribution Data
3σ error for each constant is also shown.

Extracted species	Equilibrium constant
Hpic	$K_{\mathrm{d,Hpic}} = 1.23 \times 10^2 \quad (\pm 4 \times 10^0)$
da·Hpic	$K_{\mathrm{com,da\text{-}Hpic}} = 1.30 \times 10^1 \quad (\pm 8 \times 10^{-1})$

by an increase in the diamide (**da**) concentration, which causes a decrease in the pic$^-$ concentration in the aqueous phase. This is due to complex formation between **da** and Hpic. On the other hand, the extraction of HNO_3 with **da** was found to be negligible when the aqueous HNO_3 concentration was not higher than 0.1 mol dm^{-3}. On the basis of Eq. 12, the value of the equilibrium constant for the complex formation between **da** and Hpic, $K_{\mathrm{com,da\text{-}Hpic}}$, can be obtained. If the concentration of Hpic extracted as its complex with **da** into the organic phase is negligible, as against $[\mathbf{da}]_{\mathrm{org,t}}$, the free **da** concentration in the organic phase, $[\mathbf{da}]_{\mathrm{org}}$, can be regarded as being equal to $[\mathbf{da}]_{\mathrm{org,t}}$; see the next paragraph. In this case, the data analysis can be made much more simply by using $[\mathbf{da}]_{\mathrm{org,t}}$ as a substitute for $[\mathbf{da}]_{\mathrm{org}}$ in Eq. 12. The left side of this equation was plotted against $\{H^+\}\{\mathrm{pic}^-\}$ at a fixed **da** concentration (0.1 mol dm^{-3}). If the combination number of Hpic, n, is one, the left-hand side value is independent of $\{H^+\}\{\mathrm{pic}^-\}$. In fact, the experimental results in Fig. 9 show this case. The left-side value was also plotted against the **da** concentration at various aqueous HNO_3 concentrations (0.005, 0.05, and 0.1 mol dm^{-3}) at a fixed Hpic concentration (0.01 mol dm^{-3}), as shown in Fig. 10. This value is independent of $[HNO_3]_t$, which is evident from the fact that $n = 1$, and thus $(K_{\mathrm{d,Hpic}}\{H^+\}\{\mathrm{pic}^-\})^{n-1} = 1$. As a result, a single line having slope of one was obtained, which means that the combination number of **da**, m, is also one. From these, only a 1 : 1 complex between **da** and Hpic is concluded to form in the organic phase. The thus-obtained value of $K_{\mathrm{com,da\text{-}Hpic}}$ is shown in Table 2.

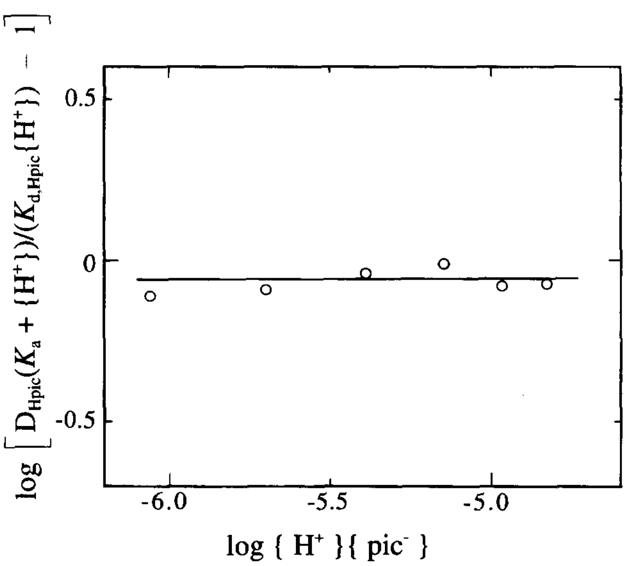

Fig. 9. $D_{\mathrm{Hpic}}(K_a + \{H^+\})/(K_{\mathrm{d,Hpic}}\{H^+\}) - 1$ as a function of $\{H^+\}\{\mathrm{pic}^-\}$ when $[\mathbf{da}]_{\mathrm{org,t}}$ is fixed at 0.1 mol dm^{-3}; $[HNO_3]_t$ = 0.001mol dm^{-3} = const, $[\mathrm{Hpic}]_{\mathrm{init}}$ = 0.01—0.1 mol dm^{-3}.

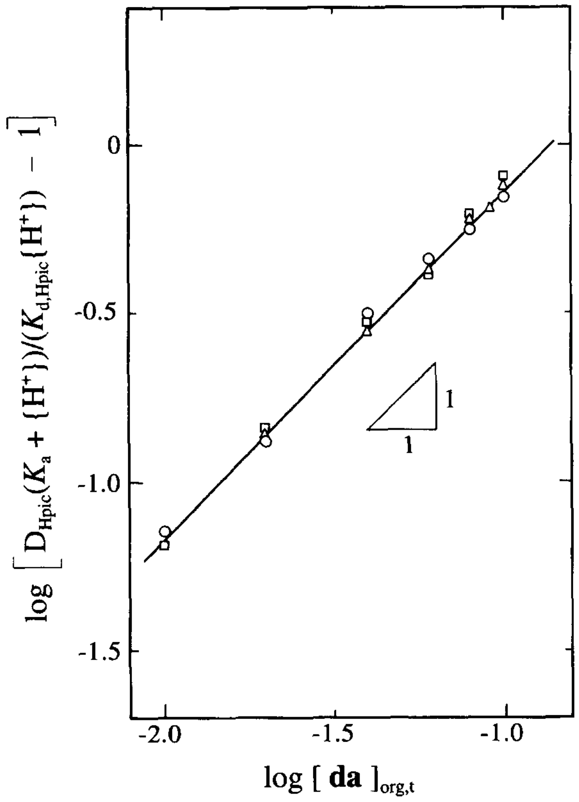

Fig. 10. $D_{\mathrm{Hpic}}(K_a + \{H^+\})/(K_{\mathrm{d,Hpic}}\{H^+\}) - 1$ as a function of $[\mathbf{da}]_{\mathrm{org,t}}$ when $[\mathrm{Hpic}]_{\mathrm{init}}$ is fixed at 0.01 mol dm^{-3}; $[HNO_3]_t$ = ○ 0.005, △ 0.05, □ 0.1 mol dm^{-3}.

Free Diamide Concentration. By means of liquid chromatography, the distribution of **da**, itself, to aqueous HNO_3 solutions was found to be negligible when $[HNO_3]_t \leqq 0.1$ mol dm^{-3}; i.e., the concentration of **da** in the aqueous phase was always lower than 10^{-5} mol dm^{-3} when the concentration of **da** initially added to the liquid-liquid system, $[\mathbf{da}]_{\mathrm{init}}$, was 0.1 mol dm^{-3}. Thus, the total concentration of **da** in the organic phase, $[\mathbf{da}]_{\mathrm{org,t}}$, can be regarded as being equal to $[\mathbf{da}]_{\mathrm{init}}$. The distribution of HNO_3 to the organic phase was also checked by using ion chromatography for back-extracted NO_3^- into an aqueous NaOH solution. The amount of the extracted HNO_3 by **da** into the organic phase was found to be only a trace in the aqueous HNO_3 concentration range of the present study. Thus, the reduction in the free **da** concentration by complexation between **da** and HNO_3 was also negligible. Furthermore, no dimerization of **da** in the organic phase (benzene) has been observed,[17] and the amount of **da** complexed with Eu(III), whose initial concentration is 6.6×10^{-6} mol dm^{-3}, was also negligible as against $[\mathbf{da}]_{\mathrm{org,t}}$. From these results, the concentration of **da** free from Eu(III), Hpic, HNO_3, and **da** itself in the organic phase, $[\mathbf{da}]_{\mathrm{org}}$, could be calculated by taking account of only the **da**–Hpic complexation.

From the result that **da** formed only a 1 : 1 complex with

Hpic, the free **da** concentration in the organic phase can be written as:

$$[\mathbf{da}]_{\mathrm{org}} = \frac{[\mathbf{da}]_{\mathrm{org,t}}}{1 + K_{\mathrm{com,}\mathbf{da}\text{-}\mathrm{Hpic}} K_{\mathrm{d,Hpic}}[\mathrm{Hpic}]} . \tag{13}$$

Here, from the values of $K_{\mathrm{com,}\mathbf{da}\text{-}\mathrm{Hpic}}$ and $K_{\mathrm{d,Hpic}}$ shown in Table 1,

$$K_{\mathrm{com,}\mathbf{da}\text{-}\mathrm{Hpic}} K_{\mathrm{d,Hpic}}[\mathrm{Hpic}] \leqq 0.07 << 1 , \tag{14}$$

on condition that $[\mathrm{Hpic}]_{\mathrm{init}} \leqq 0.01$ mol dm^{-3} and $[\mathrm{HNO_3}]_{\mathrm{t}} \leqq 0.1$ mol dm^{-3}; $[\mathrm{Hpic}] \leqq 4.3\times10^{-5}$ mol dm^{-3} under the condition. Thus, $[\mathbf{da}]_{\mathrm{org}}$ in Eq. 13 is roughly equal to $[\mathbf{da}]_{\mathrm{org,t}}$. Hence, in fact, all analyses of the experimental data in the present study were made by regarding $[\mathbf{da}]_{\mathrm{org,t}}$ ($\approx[\mathbf{da}]_{\mathrm{init}}$) as $[\mathbf{da}]_{\mathrm{org}}$.

Activity of Diamide and Picric Acid in Organic Phase. The change in the activity coefficient of an extractant in nonpolar solvents can be due to mainly the hydration of the extractant and the association of the extractant, itself (dimerization, trimerization, etc).[13,18—21] The hydration and association of **da** was preexperimentally checked on the basis of the water distribution to benzene[17] by a similar manner to that in previous studies.[13,18—20] From the experimental results, no **da** association in the organic phase occurred, and only a single hydrate of $\mathbf{da}\cdot\mathrm{H_2O}$, which formed stoichiometrically, was found, at least, up to $[\mathbf{da}]_{\mathrm{org,t}} = 0.1$ mol dm^{-3} in benzene. When $[\mathrm{HNO_3}]_{\mathrm{t}} \leqq 0.1$ mol dm^{-3}, i.e., $a_{\mathrm{w}}\approx1$, the mixture of the anhydrous **da**, **da**(anhy), and the **da** monomer monohydrate can apparently be treated as one species, because $[\mathbf{da}]_{\mathrm{org}}$ is nearly in proportion to $[\mathbf{da}(\mathrm{anhy})]_{\mathrm{org}}$ at $a_{\mathrm{w}}\approx1$; $[\mathbf{da}]_{\mathrm{org}} = [\mathbf{da}(\mathrm{anhy})]_{\mathrm{org}} + [\mathbf{da}\cdot\mathrm{H_2O}]_{\mathrm{org}} = (1 + K_{\mathbf{da}\text{-}\mathrm{w}} a_{\mathrm{w}})[\mathbf{da}(\mathrm{anhy})]_{\mathrm{org}}$, where $K_{\mathbf{da}\text{-}\mathrm{w}} = [\mathbf{da}\cdot\mathrm{H_2O}]_{\mathrm{org}}/[\mathbf{da}(\mathrm{anhy})]_{\mathrm{org}} a_{\mathrm{w}}$. From these results, no activity correction for the **da** concentration in the organic phase was made in the data analyses of the present study. In fact, the experimental results in Figs. 3, 7, and 10, each of which shows a straight line having a consistent slope, should not imply the necessity of an activity correction for the **da** concentration.

On the other hand, no dimer of Hpic was also found in the organic phase in the Hpic concentration range of the present study ($\leqq 0.1$ mol dm^{-3}), as can be seen from Fig. 8. Furthermore, the hydration of Hpic does not have to be taken into account for the same reason as in the case of **da** when $[\mathrm{HNO_3}]_{\mathrm{t}} \leqq 0.1$ mol dm^{-3}, i.e., $a_{\mathrm{w}}\approx1$. Hence, no activity correction for Hpic in the organic phase should also be necessary under the condition of the present study.

Effect of Hydrophobic Anion as Counter Ion. In the comparison of $K_{\mathrm{ex,}\mathbf{da}}$ and $K_{\mathrm{ex,}\mathbf{da}\text{-}\mathrm{Hpic}}$ shown in Table 1, the difference between these two extraction equilibrium constants is only the difference of the counter ion, i.e., $\mathrm{NO_3}^-$ or pic^-; the coordination property between Eu(III) and **da** can be a common factor to these constants, since $x = p = 2$. However, because these values are very different, the effect of the hydrophobic counter anion is surprisingly strong. The magnitude of $K_{\mathrm{ex,}\mathbf{da}\text{-}\mathrm{Hpic}}$ is about sixty billion times larger than that of $K_{\mathrm{ex,}\mathbf{da}}$, which should be the origin of the extremely strong cooperative effect; but the cause of the largeness of $K_{\mathrm{ex,}\mathbf{da}\text{-}\mathrm{Hpic}}$ is not yet clear. A more detailed study concerning the effect of hydrophobicity of the counter ion on such an ion-pair extraction is necessary for a complete understanding.

Conclusions

1. The extraction of Eu(III) with the diamide (**da**) was very much enhanced by the addition of picric acid (Hpic); a strong cooperative effect of **da** and Hpic (anion effect) occurred.

2. The ion-pair, $[\mathrm{Eu}(\mathbf{da})_2](\mathrm{pic})_3$, extraction equilibrium caused the cooperative effect.

3. The extraction equilibrium constant of $[\mathrm{Eu}(\mathbf{da})_2](\mathrm{pic})_3$ was about 6×10^{10} times larger than that of $[\mathrm{Eu}(\mathbf{da})_2](\mathrm{NO_3})_3$, which should be the origin of the extremely strong cooperative effect.

4. The extraction of ion-pairs containing $\mathrm{NO_3}^-$, i.e., $[\mathrm{Eu}(\mathbf{da})_2](\mathrm{NO_3})_3$, $[\mathrm{Eu}(\mathbf{da})_2](\mathrm{pic})(\mathrm{NO_3})_2$, and $[\mathrm{Eu}(\mathbf{da})_2](\mathrm{pic})_2(\mathrm{NO_3})$, was practically negligible as against the $[\mathrm{Eu}(\mathbf{da})_2](\mathrm{pic})_3$ extraction.

5. The reduction of the cooperative effect by an increase in the aqueous $\mathrm{HNO_3}$ concentration was due to a decrease in the pic^- concentration in the aqueous phase.

6. The diamide formed a 1 : 1 complex with picric acid in the organic phase, which also caused a decrease in the pic^- concentration in the aqueous phase.

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