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Water Molecules in Organic Solvents Involved in the Synergistic Extraction of Europium(Ⅲ) with β-Diketones and Lewis Bases

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To explain the difference in the magnitude of synergistic extraction among organic solvents, the water solubility in hexane, carbon tetrachloride, benzene, and chloroform was measured, and then the residual hydration number of europium(Ⅲ) in the β-diketonato chelate and in their adducts with 1,10-phenanthroline as well as the adduct formation constants were determined. Using the data, the formation constants of the adduct according to a novel definition, in which the water concentration in the organic phase is treated as one variable, were determined. The constants are approximately constant irrespective of the organic solvents, although those according to the conventional definition are different among the solvents. It has been concluded that one of the most important factors controlling the magnitude of synergistic effects is the presence of water, such as the water content dissolved in organic solvents, and the hydration and dehydration of the relevant species, because water molecules compete with a Lewis base in complexation to the metal(Ⅲ) chelates in the organic solvents.

A remarkable enhancement of the extraction efficiency of lanthanoids(Ⅲ) in the extraction with a mixture of a β-diketone and a Lewis base, the so-called synergistic effect, is known to be caused by adduct formation of the Lewis base to lanthanoid(Ⅲ)β-diketonato chelates.[1] The extraction efficiency of a certain lanthanoid(Ⅲ) is different among different organic solvents; the adduct formation constants of tris(thenoyltrifluoroacetonato)europium(Ⅲ), [Eu(tta)$_3$], with trioctylphosphine oxide (TOPO)[2] and with tributyl phosphate (TBP)[3] in organic solvents having larger solubility parameters are smaller than in those having smaller ones. It has also been reported that the adduct formation constants of [Eu(tta)$_3$] are larger in organic solvents having lower water solubility.[4,5] The magnitude of adduct formation constants has also been discussed in connection with the polarity of solvents.[5]

In solvent-extraction systems, since the organic phase is always saturated with water, the water should be involved in the complexation in organic solvents or synergistic effects. Accordingly, it should be valuable for solution chemistry as well as separation chemistry to elucidate the effect of water in organic solvents on the synergistic effects.

The present work was aimed to investigate the involvement of water molecules in organic solvents in the synergistic effect.

Experimental

Reagents. All reagents were of analytical grade. 1,10-Phenanthroline (phen) was obtained from Kanto Chemicals (Tokyo) as monohydrate. Chloroform was washed three times with deionized water prior to use. The other reagents were used without purification.

1,1,1-Trifluoro-5,5-dimethyl-2,4-hexanedione (pivaloyltrifluoroacetone; PTA = Hpta : HA) was obtained from Dojindo Laboratories (Kumamoto). Europium(Ⅲ) oxide was obtained from Mitsuwa Chemicals (Osaka). For Karl Fischer coulometric titration, HYDRANAL Coulomat AK as the anolyte, serving as a generator of I$_2$, and HYDRANAL Coulomat CG-K as catholyte were obtained from Riedel-de Haën (Seelze, Germany).

Procedure. Most experiments were performed in a thermostated room at 298 K.

(i) Determination of the Distribution Constant of 1,10-Phenanthroline. An organic solution (CHCl$_3$, C$_6$H$_6$, and CCl$_4$) of phen at 5×10^{-4} M (1 M = 1 mol dm^{-3}), 5.0 mL, and 0.1 M (H, Na)ClO$_4$, 10.0 mL were placed in a stoppered glass tube. The mixed solutions were vigorously shaken for an hour to attain the distribution equilibrium. After centrifuging both phases for a few minutes, the absorbance in the organic phase at 300 nm was measured to determine the concentration of phen remaining in the organic phases. The wavelength was not a peak, but was chosen to avoid any overlapping of the absorbance from the organic solvents. Separately, into a portion of 5 mL taken from the aqueous phases, 1 mL of sodium hydroxide solution (1×10^{-3} M) was added, and the phen was re-extracted into 5 mL of chloroform. From the absorbance in the organic phase, the concentration of phen in the aqueous phase was determined. Upon determining the distribution constant of phen between 0.1 M NaClO$_4$ and hexane, the absorbance in the aqueous phase was directly measured at 264.2 nm after the solution was adjusted to be basic. The concentration of phen in the organic phase was determined by measuring the absorbance at an absorption maximum wavelength of phen, 271.6 nm, after back-extraction into 0.01 M HClO$_4$ (μ = 0.1).

The concentration ratio between both phases was defined as the distribution ratio of phen.

(ii) Determination of the Adduct Formation Constants of [Eu(pta)$_3$] with 1,10-Phenanthroline. The procedure was performed in a similar way to that described elsewhere.[6] An aqueous solution containing europium(Ⅲ) (2.0×10^{-4} M–1.2×10^{-3} M) adjusted the total ion concentration to 0.1 M with a sodium perchlorate aqueous solution, 8.0 mL, was shaken with an identical volume of an organic solution containing PTA (0.05 M–0.2 M)

Table 1. Distribution Constants and Acid Dissociation Constants of 1,10-Phenanthroline and PTA

		$CHCl_3$	C_6H_6	CCl_4	C_6H_{14}
phen	pK_a	4.77 ± 0.02[6]			
	$\log K_d$	2.72 ± 0.02	0.76 ± 0.05	0.11 ± 0.04	-1.24 ± 0.01
PTA[10]	pK_a	7.01			
	$\log K_d$	2.51	2.15	2.15	1.87

and phen ($< 5.0 \times 10^{-3}$ M). The hydrogen ion concentration in the aqueous phase was measured potentiometrically using 1.00×10^{-2} M perchloric acid at 0.1 M (H, Na)ClO_4 as a standard of pC_H 2.00 ($pC_H = -\log[H^+]$). The europium(III) concentration in the organic phase was measured by ICP-AES (inductively coupled plasma atomic emission spectrometry; HITACHI P-4000) after back-extraction into 0.1 M perchloric acid. The concentration of europium(III) in aqueous phases was calculated by subtracting the concentration of europium(III) transferred into the organic phase from the initial concentration in the vial.

(iii) The Residual Hydration Numbers of Europium(III) in the Pta-Chelate and Its Adducts with Phen. Tris(pivaloyltrifluoroacetonato)europium(III) was prepared by two methods, i.e., by synthesis and solvent-extraction techniques. The europium(III) chelate was principally prepared in a similar way to that described elsewhere.[7,8] The obtained crystal was dissolved in organic solvents to be 1.5×10^{-3} M–2×10^{-2} M, and the solution was shaken with a 0.1 M $NaClO_4$ aqueous solution for 1 h to saturate the solutions with water. The solvent extraction was performed as follows: a 0.05 M europium(III) perchlorate solution, 6 mL, was shaken at pC_H 5–6 with an identical volume of a solution containing 0.1 M PTA for 1 hour.

The adduct of $[Eu(pta)_3]$ with phen was prepared by three ways: one was performed by mixing 6 mL of an europium(III) perchlorate aqueous solution (6×10^{-3} M) at pC_H 5.0-5.5 with an equal volume of organic solution (C_6H_6 or CCl_4) containing PTA (1.7×10^{-2} M) and phen (7.0×10^{-3} M). Upon preparing the adduct in hexane, the hexane containing 4.0×10^{-3} M PTA and an aqueous solution containing 2.0×10^{-3} M phen and europium(III) perchlorate solution (1.2×10^{-3} M–1.7×10^{-3} M) were employed. The second method was performed by directly dissolving the crystal of $[Eu(pta)_3{\cdot}phen]$ in organic solvents. The crystal was prepared in a similar way to that reported previously.[9] The third method was performed by mixing the solution of dissolved $[Eu(pta)_3]$ crystal with a phen solution; a solution ($CHCl_3$, C_6H_6, or CCl_4) of dissolved $[Eu(pta)_3]$ crystal (0.01 M–0.015 M) was mixed with a phen solution (8×10^{-3} M–1.5×10^{-2} M), and the mixture was shaken with 0.1 M sodium perchlorate aqueous solution. The hexane solution was prepared by shaking the pta-chelate (1.5×10^{-3} M) solution with a 0.1 M $NaClO_4$ aqueous solution containing 2×10^{-3} M phen at pC_H ca. 5.5.

A portion of the organic phase was transferred into another tube and the water concentration was measured by Karl Fischer coulometric titration (Hiranuma Sangyo Model AQ-7, Ibaraki, Japan). The europium(III) concentration was also measured by ICP-AES after back-extraction with 0.1 M perchloric acid.

Results and Discussion

(i) Distribution Constants of 1,10-Phenanthroline. When log *D* of phen (B) was plotted against pC_H, the plot showed two asymptotes; one was flat to the X-axis and the other was a straight line having a slope of one. The distribution ratio can thus be represented as

$$D = \frac{[B]_o}{[B]+[HB^+]} = \frac{K_d}{1+\dfrac{[H^+]}{K_a}}, \tag{1}$$

where "o" denotes the organic phases and the lack of "o" denotes the aqueous phase. The K_d ($K_d = [phen]_o/[phen]$) is the distribution constant of phen. The data were analyzed using Eq. 1 and pK_a ($K_a = [H^+][B]/[HB^+]$).[6] The values of the obtained equilibrium constants are summarized in Table 1 together with those for PTA.[10]

(ii) The Formation Constants of 1,10-Phenanthroline Adducts to $[Eu(pta)_3]$. The formation constants of the $[Eu(pta)_3]$ adduct with 1,10-phenanthroline in the organic solutions were determined in a similar way to that described elsewhere.[6] The total concentration of phen in the vial, B_T, can be represented as

$$B_T = [B] + [BH^+] + [B]_o + [Eu^{III}]_{o,T}. \tag{2}$$

As reported before,[6] because the adduct is very stable, $[EuA_3{\cdot}B]_o$ can be regarded as the total Eu^{III} concentration in the organic phase, $[Eu^{III}]_{o,T}$. Then, $[B]_o$ is calculated based on

$$B_T = [B]_o\{1 + (1 + [H^+]/K_a)/K_d\} + [Eu^{III}]_{o,T}. \tag{2'}$$

Figure 1 shows the enhancement of the distribution ratio of

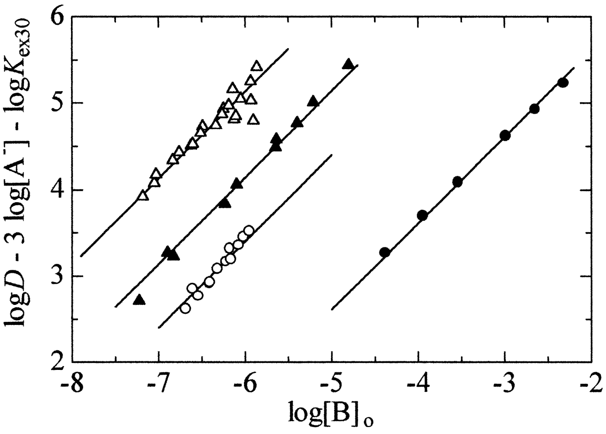

Fig. 1. The change in the distribution ratio (*D*) of europium(III) between 0.1 M $NaClO_4$ aqueous solution and an organic solution containing PTA as a function of phen concentration at equilibrium: $CHCl_3$ ●, C_6H_6 ○, CCl_4 ▲, C_6H_{14} △.

Table 2. The Extraction Constants of [Eu(pta)$_3$], Adduct Formation Constant of [Eu(pta)$_3$] with Phen, and the Saturated Solubility of Water in the Organic Solvents at 298 K

	$CHCl_3$	C_6H_6	CCl_4	C_6H_{14}
log K_{ex30}	18.13 ± 0.05	18.29 ± 0.07	17.58 ± 0.12	16.74 ± 0.14
log $\overline{\beta}_1$	7.61 ± 0.06	9.40 ± 0.09	10.14 ± 0.15	11.12 ± 0.20
Water solubility in pure organic solvents /M	$(7.2 \pm 0.2) \times 10^{-2}$	$(3.8 \pm 0.1) \times 10^{-2}$	$(8.5 \pm 0.3) \times 10^{-3}$	$(3.5 \pm 0.4) \times 10^{-3}$

$K_{ex30} = [EuA_3]_o[Eu^{3+}]^{-1}[A^-]^{-3}$, $\overline{\beta}_1 = [EuA_3{\cdot}B]_o[EuA_3]_o^{-1}[B]_o^{-1}$.

europium(III) in the presence of phen. Since the plot gives a straight line with a slope of 1, the stoichiometry between [Eu(pta)$_3$] and phen can be regarded as 1 : 1, as expected.

Then, the distribution ratio of europium(III) in the phen concentration region in Fig. 1 can be represented as

$$D = \frac{[EuA_3{\cdot}B]_o}{[Eu^{3+}]} = K_{ex30}[A^-]^3\overline{\beta}_1[B]_o, \tag{3}$$

where

$$K_{ex30} = [EuA_3]_o[Eu^{3+}]^{-1}[A^-]^{-3}, \tag{4}$$

$$\overline{\beta}_1 = [EuA_3{\cdot}B]_o[EuA_3]_o^{-1}[B]_o^{-1}, \tag{5}$$

and [A$^-$] is calculated from the following equation:

$$\begin{aligned} A_T &= [HA] + [A^-] + [HA]_o + 3[EuA_3{\cdot}B]_o, \\ &= [A^-]\{1 + [H^+](1 + K_d)/K_a\} + 3[Eu^{III}]_{o,T}, \end{aligned} \tag{6}$$

The values of $\overline{\beta}_1$ were determined according to Eq. 3 using the data in Fig. 1.

The adduct formation constants obtained are summarized in Table 2 together with the water solubility in organic solvents. The order of the formation constants of the adduct also decreases inversely to the order of the increase in the water solubility, as pointed out before.[4]

Although it was reported that [Eu(tta)$_3$] coordinated phen of two molecules as well as one in toluene, benzene, carbon tetrachloride, and cyclohexane,[5] in the present work the formation constant of [Eu(pta)$_3$·2phen] could not be determined within the experimental accuracy in all of the solvents studied. Separately, in the absence of phen, the distribution ratio of europium(III) was measured with a given concentration of PTA at different values of pC_H (3.1–4.3), and also with different PTA concentrations (0.05 M–0.2 M) at a given pC_H. When the log $D[H^+]^3$ was plotted as a function of log [HA]$_o$ as well as log $D/[HA]_o^3$ vs pC_H, straight lines having slopes of +3 were obtained. From the data the extraction constants, K_{ex30}, were determined. The values of K_{ex30} are also listed in Table 2.

(iii) The Residual Hydration Number of Europium(III) in the Pta-Chelate and Its Phen Adduct in Organic Solvents. As reported before,[7,8] when europium(III) is extracted with PTA, the total water content in the organic phase should consist of water molecules accompanied by PTA, itself, and [Eu(pta)$_3$] as well as the water content dissolved in the pure organic solvents, $[H_2O]_{solv}$; actually, however, the content of water accompanied with PTA would be negligible.[8] Figure 2 shows the water concentration in benzene and hexane into which Eu^{III} was extracted with PTA. As can be seen from Fig. 2, with increasing the concentration of the extracted Eu^{III}, the concentration of water in the organic phase increases. The water concentration at the intercept gives the water solubility in pure organic solvents. Then, the residual hydration numbers were obtained by dividing the increment of water content, $[H_2O]_{o,T} - [H_2O]_{solv}$, by the concentration of [Eu(pta)$_3$] in the organic phase at equilibrium.

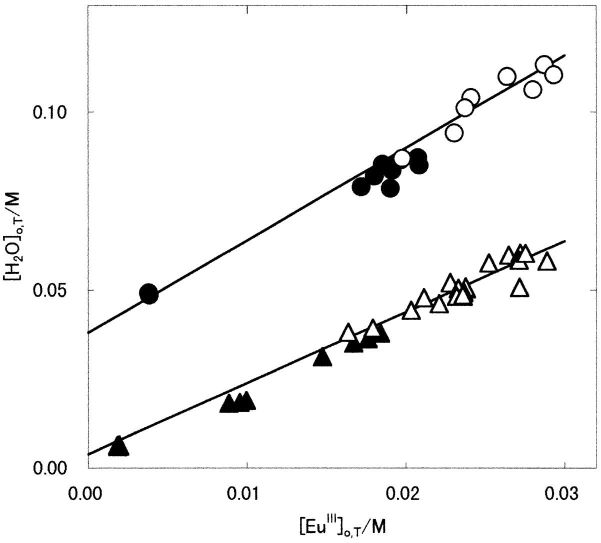

Fig. 2. Correlation between the concentration of water transferred into benzene (circles) and hexane (triangles), and the concentration of [Eu(pta)$_3$] prepared by synthesis (closed symbols) and solvent extraction (open symbols). The solid lines are calculated from $[H_2O]_{o,T} = S + n_0[EuA_3]_o$ where n_0 is the residual hydration number obtained from the data using [Eu(pta)$_3$] prepared by solvent extraction, and S is the concentration of water saturated in the pure organic solvents.

Table 3. Residual Hydration Number of Eu^{III} in [Eu(pta)$_3$] Obtained by Solvent Extraction and Synthesis

	Solvent extraction	Synthesis
$CHCl_3$[8]	2.40 ± 0.03	2.50 ± 0.08
C_6H_6	2.50 ± 0.08	2.46 ± 0.13
CCl_4	2.19 ± 0.03	1.75 ± 0.20
C_6H_{14}	2.09 ± 0.05	1.59 ± 0.24

Since there is uncomplexed PTA in the organic phase in sol-

Table 4. The Water Content in Benzene Containing [Eu(pta)$_3$·phen] and Saturated Water Solubility

a. Prepared by solvent extraction methods

Experimental condition				Concentration at equilibrium			
$[\mathrm{Eu^{III}}]_T/10^{-2}$ M	$[\mathrm{PTA}]_T/10^{-2}$ M	$[\mathrm{phen}]_T/10^{-3}$ M	pC_H	$[\mathrm{Eu^{III}}]_{o,T}/10^{-3}$ M	$[\mathrm{H_2O}]_{o,T}/10^{-2}$ M	$[\mathrm{H_2O}]_{C6H6}/10^{-2}$ M	n_1
1.02_3	1.67_3	6.74_0	3.7_6	5.55_9	3.71_3	3.77_4	−0.11
1.02_3	1.67_3	6.74_0	3.7_0	5.76_0	3.81_7		0.07
1.02_3	1.67_3	6.74_0	3.7_4	5.71_6	3.80_0		0.05
1.02_3	1.67_3	6.74_0	3.7_3	5.83_9	3.73_6		−0.07
1.02_3	1.67_3	6.74_0	3.7_2	5.93_5	3.81_2		0.06
1.02_3	1.67_3	6.74_0	3.7_2	5.62_5	3.81_1		0.07

b. Prepared by mixing [Eu(pta)$_3$] solution with phen solution

Experimental condition		Concentration at equilibrium		
$[\mathrm{Eu^{III}}]_{o,T}/10^{-3}$ M	$[\mathrm{phen}]_T/10^{-2}$ M	$[\mathrm{H_2O}]_{o,T}/10^{-2}$ M	$[\mathrm{H_2O}]_{C6H6}/10^{-2}$ M	n_1
3.99_1	6.01_5	3.76_2	3.75_6	0.02
4.02_1	6.01_5	3.71_2		−0.11
4.06_0	6.01_5	3.76_6		0.02
3.88_5	6.01_5	4.09_4	4.07_0	0.06
3.81_6	6.01_5	4.09_6		0.07
3.94_7	6.01_5	4.09_2		0.06

c. Prepared by dissolving [Eu(pta)$_3$·phen] crystal

Experimental condition	Concentration at equilibrium		
$[\mathrm{Eu^{III}}]_{o,T}/10^{-3}$ M	$[\mathrm{H_2O}]_{o,T}/10^{-2}$ M	$[\mathrm{H_2O}]_{C6H6}/10^{-2}$ M	n_1
5.85_7	3.83_9	3.86_5	−0.04
5.93_0	3.86_8		0.00
5.82_2	3.86_8		0.00
5.94_4	3.82_7		−0.06
5.86_1	3.84_6		−0.03

vent extraction, the residual hydration numbers of pta-chelates (n_0) were more directly reconfirmed using a solution of dissolved [Eu(pta)$_3$] crystals.

The hydration numbers determined by the two methods are listed in Table 3. The order of the residual hydration numbers of the pta-chelates among organic solvents is similar to that of the water solubility. The values of n_0 obtained using the [Eu(pta)$_3$] crystal seem to be slightly smaller than those obtained from solvent extraction.

The hydration numbers of [Eu(pta)$_3$·phen] were determined in a similar way to the determination of the residual hydration number of [Eu(pta)$_3$].

Table 4 gives typical data used to determine the residual hydration number of europium(III) in the phen adduct to the pta-chelate in benzene. Table 4a gives the data obtained using [Eu(pta)$_3$·phen] prepared by the solvent extraction of europium(III) with PTA and phen. Tables 4b and 4c give data obtained by using the solutions obtained with mixing the benzene solution dissolved [Eu(pta)$_3$] chelate with the phen solution, and with the direct dissolution of [Eu(pta)$_3$·phen] crystal, respectively. The reproducibility with Karl Fischer coulometric titration was checked by measuring the concentration of water saturated in pure organic solvents at each titration run. As can be seen in Table 4, the water content is not always constant in each run. However, the increment of the water content, or the reproducibility of the balance of water content in the presence of the chelate from that in the absence is quite good. Similar experiments were performed in chloroform, carbon tetrachloride, and hexane. All of the procedures were repeated in several runs.

The hydration numbers of the phen adduct, n_1, are summarized in Table 5. In all of the organic solutions, regardless of the preparation method of the adducts, the hydration numbers of [Eu(pta)$_3$·phen] were almost zero. This may suggest that almost all of the hydrated molecules would be released from europium(III) upon the formation of the adducts.

(iv) A Novel Definition for the Equilibrium Constants in Organic Solvents Saturated Water. In general, the term of the water concentration is excluded from the equilibrium constant in complexation in organic solutions, as represented by Eq. 3, because the involvement of water molecules in organic solvents has not been treated in the complexation in the organic phases.

However, more precisely, the equilibrium should be written

Table 5. Residual Hydration Number of Eu^{III} in Phen Adduct to $Eu(pta)_3$ (n_1) Prepared by Three Methods

	Solvent extraction method	Mixing of $[Eu(pta)_3]$ and phen solutions	$[Eu(pta)_3\cdot phen]$ crystal
$CHCl_3$	0.12 ± 0.02[9]	0.02 ± 0.16	0.09 ± 0.11
C_6H_6	0.09 ± 0.11	0.02 ± 0.22	0.00 ± 0.05
CCl_4	0.04 ± 0.02	0.07 ± 0.05	0.01 ± 0.07
C_6H_{14}	0.00 ± 0.15	0.00 ± 0.01	0.02 ± 0.10

Table 6. Formation Constants of Phen Adduct to $[Eu(pta)_3]$ According to Conventional Definition ($\log \overline{\beta}_1$) and Proposed Definition ($\log K_1$)

	$\log K_1$
$CHCl_3$	4.9 ± 0.06
C_6H_6	5.9 ± 0.10
CCl_4	5.6 ± 0.15
C_6H_{14}	6.1 ± 0.20

$K_1 = [EuA_3\cdot B]_o[H_2O]_o^{n_0}0[EuA_3\cdot n_0H_2O]_o^{-1}[B]_o^{-1}$.

as follows:

$$LnA_3\cdot n_0H_2O_{(o)} + mL\cdot sH_2O_{(o)} \rightleftarrows LnA_3\cdot mL\cdot n_mH_2O_{(o)} + (n_0+ms-n_m)H_2O_{(o)} \tag{7}$$

$$K_m = \frac{[LnA_3\cdot mL\cdot n_mH_2O]_o[H_2O]_o^{(n_0+ms-n_m)}}{[LnA_3\cdot n_0H_2O]_o[L\cdot sH_2O]_o^m} \tag{7'}$$

Therefore, the relation between $\overline{\beta}_m$ and K_m should be represented as

$$K_m = \overline{\beta}_m[H_2O]_o^{(n_0+ms-n_m)} \tag{8}$$

Under the present experimental conditions, the organic phase is saturated with water. Since it is possible to use the solubility in organic solvents in the term of water concentration in Eq. 8, as suggested before,[11] and the numbers of "s"[8] and "n_m" are almost zero, respectively, the terms of ($n_0 + ms - n_m$) can be regarded as n_0, which are listed in Table 3. Table 6 gives the formation constants of phen adducts to the pta-chelate according to the definition proposed in the present study, K_1. Although the number of $\overline{\beta}_1$ differs greatly among organic solvents, the numbers of K_1 are similar to each other.

The present results suggest that the difference in the magnitude of the synergistic effect among organic solvents is mainly caused by the different water solubilities in organic solvents, because the higher concentration of water should make the adduct formation equilibria move to the left side in Eq. 7.

Regarding chloroform, the constant seems to be a little different from the others. This difference may be caused by the interaction between $CHCl_3$ and phen or the pta-chelate due to the active hydrogen atom in the chloroform molecule.

It has been reported[4,12,13] that the adduct-formation constants represented by the activity units were independent from organic solvents, when the activity coefficients of the relevant species were calculated from the corresponding solubility parameters based on regular solution theory. Accordingly, the coincidence of the present results with their conclusion suggests that the change in activities can be explained in terms of a chemical equilibrium.

In conclusion, it may be derived from the present results that all of the phenomena observed in solutions which have not yet been explained stoichiometrically, such as the solvent effects and the change in the activity coefficients, can be explained in terms of stoichiometrical equilibria, when all of the relevant equilibria are analyzed in detail.

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References

1 T. Sekine and Y. Hasegawa, "Solvent Extraction Chemistry", Marcel Dekker, New York, (1978).

2 K. Akiba, M. Wada, and T. Kanno, *J. Inorg. Nucl. Chem.*, **43**, 1031 (1981).

3 K. Akiba, *J. Inorg. Nucl. Chem.*, **35**, 2525 (1973).

4 Y. Hasegawa, T. Nakano, and G. R. Choppin, *Solv. Extr. Ion Exch.*, **1**, 745 (1983).

5 K. Farah and A. T. Kandil, *J. Radioanal. Nucl. Chem.*, **157**, 177 (1992).

6 S. Yajima and Y. Hasegawa, *Bull. Chem. Soc. Jpn.*, **71**, 2825 (1998).

7 Y. Hasegawa, E. Ishiwata, T. Ohnishi, and, G. R. Choppin, *Anal. Chem.*, **71**, 5060 (1999).

8 Y. Hasegawa, M. Miratsu, T. Kondo, *Inorg. Chim. Acta*, **303**, 291 (2000).

9 Y. Hasegawa, M. Miratsu, G. R. Choppin, *Anal. Chim. Acta*, **428**, 149 (2001).

10 T. Sekine, Y. Hasegawa, and N. Ihara, *J. Inorg. Nucl. Chem.*, **35**, 3968 (1973).

11 I. Matsubayashi, A. Inagaki, and Y. Hasegawa, to be published in *Bunseki Kagaku.*

12 K. Akiba, N. Suzuki, and T. Kanno, *Bull. Chem. Soc. Jpn.*, **42**, 2537 (1969).

13 S. Nakamura, H. Imura, and N. Suzuki, *Inorg. Chim. Acta*, **109**, 157 (1985).