Inorganica Chimica Acta, *110* (1985) 101–105

Synergic Extraction of Thulium(III) with Thenoyltrifluoroacetone and Neutral Unidentate and Bidentate Heterocyclic Amines

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Received March 11, 1985

Abstract

Synergic extraction of thulium(III) with 2-thenoyltrifluoroacetone(Htta) and neutral bidentate heterocyclic amine, such as 1,10-phenanthroline(phen), 2,9-dimethyl-1,10-phenanthroline(dmp) and 2,2′-bipyridine(bpy), as well as unidentate amine, pyridine(py), in benzene and cyclohexane was investigated. Synergism was found to be due to formation of the ternary complex, $Tm(tta)_3S$ for the bidentate amines and $Tm(tta)_3S_2$ for py, in the organic phase, where S denotes a neutral ligand. Adduct formation constants (β_s) in all systems were determined. The values of $\beta_{s,1}$ for bidentate amines are very large and decrease in the following order: phen > bpy > dmp, and the value of $\beta_{s,1}$ for bpy is larger than that of $\beta_{s,2}$ for py.

Introduction

Synergic extraction of a metal ion with an acidic chelating agent and a unidentate neutral ligand, such as organophosphorus compounds, has been extensively studied [1]. Recently, the use of a bidentate neutral ligand as the synergist has been of interest and the analytical application for some transition metals has been reported [2–5]. In our laboratory the synergic extraction of bivalent metals with 2-thenoyltrifluoroacetone(Htta) and 1,10-phenanthroline and its derivatives has been investigated in detail [6, 7], and applied to the substoichiometric analysis [8]. Synergic extraction studies of the tervalent rare earth ions with Htta and bidentate heterocyclic amines have been reported [9, 10]; the results disagree in some points. For instance, the stoichiometric ratio of a metal chelate and a neutral ligand in the adduct is concluded from an ambiguous slope analysis to be 1:2 [9] or 1:1 [10], and the order of the magnitude of the adduct formation constants is inconsistent.

In the present paper, the synergic extraction of thulium(III) with Htta and bidentate neutral ligand, such as 1,10-phenanthroline(phen), 2,9-dimethyl-1,10-phenanthroline(dmp), and 2,2′-bipyridine(bpy) in benzene and cyclohexane is investigated in detail. The synergic effect of the bidentate ligands is compared with that of the unidentate heterocyclic amine, pyridine(py).

Experimental

Materials and Apparatus

A radioisotope, ^{168}Tm, was used as a tracer and was produced by 30–60 MeV bremsstrahlung irradiation of thulium oxide (99.99% purity) with the linear electron accelerator of Tohoku University. A radioactive Tm(III) solution was prepared by dissolving a known amount of the irradiated sample in hydrochloric acid, evaporating to dryness, and redissolving in 10^{-3} M perchloric acid solution. 2-thenoyltrifluoroacetone was purified by vacuum sublimation. Neutral ligands as guaranteed reagent grade were used as obtained. Benzene and cyclohexane were purified by ordinary methods. Unless otherwise stated, reagents used were of guaranteed reagent grade.

The γ-activity of ^{168}Tm was measured with an NaI(Tl) well-type scintillation detector connected with a single-channel analyzer. Extraction vials were shaken with a mechanical shaker at 330 strokes per minute. The pH value of the equilibrated aqueous phase was measured with a glass electrode.

Determination of Partition Coefficients (P_S) and Acid Dissociation Constants (K_{HS}) of Neutral Ligands

10 ml of an organic solution containing a known amount (10^{-5}–10^{-3} M) of a neutral ligand were shaken for 1 h with 10 ml of an aqueous solution of pH 8–10 containing 0.1 M sodium perchlorate. Concentration of the ligand in the aqueous or organic phase was determined spectrophotometrically [6], and the liquid–liquid partition coefficient, $P_S = [\bar{S}]/[S]$, where the bar denotes the organic phase

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0020-1693/85/$3.30

was calculated. The acid dissociation constant of the protonated ligand (K_{HS}) can be calculated from the following relation:

$$K_{HS} = \frac{[H^+]}{P_S/D_S - 1} \qquad (1)$$

where D_S denotes the apparent distribution ratio of the ligand, $D_S = [\bar{S}]/([S] + [HS^+])$. The acid dissociation constant, K_{HS}, was determined from a dependency of D_S on pH at pH 3–10 in the cyclohexane solvent system. These values are summarized in Table I.

TABLE I. The Acid Dissociation Constants and the Partition Coefficients of Neutral Ligands.

constant	solvent	phen	bpy	dmp	py
pK_{HS}	–[a]	5.04	4.50	5.81	5.36
$\log P_S$	cyclohexane	–0.97	1.14	0.12	–0.22
	benzene	0.78	2.05	1.79	0.51

[a] 0.1 M $NaClO_4$.

Extraction of Tm(III)

An aqueous solution (10 ml) containing 10^{-5} M Tm(III) labelled with ^{168}Tm was placed in a 50-ml extraction vial with a ground glass stopper. An organic solution (10 ml) containing 10^{-4}–10^{-2} M Htta and 10^{-5}–10^{-1} M neutral ligand was added, and the vial shaken for 1–3 h at 25 °C and then centrifuged. An aliquot was taken from each phase and the γ-activity was measured. The distribution ratio (D) of Tm(III) was obtained as the radioactivity ratio. The extraction equilibration was confirmed by the agreement between the distribution ratios of Tm(III) in forward and backward extraction. The pH of the aqueous phase was adjusted with 10^{-3}–10^{-2} M sulfanilic acid and sodium hydroxide solution, and the equilibrium pH value was measured immediately after phase separation. The buffer component less than 10^{-2} M gives no influence on the extraction of Tm(III). Ionic strength was adjusted to 0.1 with sodium perchlorate.

Theoretical

The extraction of a tervalent rare earth metal ion, M^{3+}, with a chelating extractant, HA, can be expressed as follows:

$$M^{3+} + 3\overline{HA} \rightleftharpoons \overline{MA_3} + 3H^+ \qquad (2)$$

$$K_{ex} = \frac{[\overline{MA_3}][H^+]^3}{[M^{3+}][\overline{HA}]^3} \qquad (3)$$

where K_{ex} denotes the extraction constant.

The distribution ratio of the metal, D_0, is written as follows:

$$D_0 = \frac{[\overline{MA_3}]}{[M^{3+}] + \Sigma[MA_n^{3-n}]} = \left(\frac{P_{HA}}{K_{HA}}\right)^3 K_{ex} \frac{[A^-]^3}{1 + \Sigma\beta_n[A^-]^n} \qquad (4)$$

where P_{HA} and K_{HA} are the partition coefficient and acid dissociation constant of HA, respectively, and β_n the stability constant of MA_n^{3-n} in the aqueous phase. In a region where the concentration of A^- is very low, $\Sigma\beta_n[A^-]^n$ is negligibly small, hence D_0 depends on the third power of $[A^-]$.

The distribution ratio, D, in the synergic extraction system with HA and the neutral ligand, S, is also written as follows:

$$D = \frac{[\overline{MA_3}] + \Sigma[\overline{MA_3S_m}]}{[M^{3+}] + \Sigma[MA_n^{3-n}]} = \left(\frac{P_{HA}}{K_{HA}}\right)^3 K_{ex} \frac{[A^-]^3(1 + \Sigma\beta_{s,m}[\bar{S}]^m)}{1 + \Sigma\beta_n[A^-]^n} \qquad (5)$$

where MA_3S_m is the adduct and $\beta_{s,m}$ the overall adduct formation constant for the equilibrium, $\overline{MA_3} + m\bar{S} \rightleftharpoons \overline{MA_3S_m}$. From the eqn. (4) and (5), the following equation is given:

$$D/D_0 = 1 + \Sigma\beta_{s,m}[\bar{S}]^m \qquad (6)$$

This equation can be rewritten as the next equation only if MA_3S_m is the dominant species in the organic phase:

$$\log D/D_0 = \log \beta_{s,m} + m \log [\bar{S}] \qquad (7)$$

The plots of $\log D/D_0$ against $\log [\bar{S}]$ may be a straight line with a slope of m.

Synergic extraction constant, $K_{ex,s,m}$, is defined as follows:

$$M^{3+} + 3\overline{HA} + m\bar{S} \rightleftharpoons \overline{MA_3S_m} + 3H^+$$

$$K_{ex,s,m} = \frac{[\overline{MA_3S_m}][H^+]^3}{[M^{3+}][\overline{HA}]^3[\bar{S}]^m} = K_{ex}\,\beta_{s,m} \qquad (8)$$

Results and Discussion

Extraction of Tm(III) with Htta

The extraction of Tm(III) with 10^{-3} M and 10^{-2} M Htta in benzene and cyclohexane was carried out and the plots of the logarithm of the distribution

TABLE II. The Equilibrium Constants in the Synergic Extraction of Tm(III) with Htta and the Neutral Ligand.

ligand	solvent	log K_{ex}	log $\beta_{s,1}$	log $\beta_{s,2}$	log $K_{ex,s,m}$
phen	cyclohexane	−7.67	11.76	–	4.09[a]
	benzene	−6.84	9.93	–	3.09[a]
bpy	cyclohexane	−7.67	7.57	–	−0.10[a]
	benzene	−6.84	6.58	–	−0.26[a]
dmp	cyclohexane	−7.67	5.97	–	−1.70[a]
	benzene	−6.84	4.06	–	−2.78[a]
py	cyclohexane	−7.67	3.53	6.30	−1.37[b]
	benzene	−6.84	3.02	4.32	−2.52[b]

[a] m = 1. [b] m = 2.

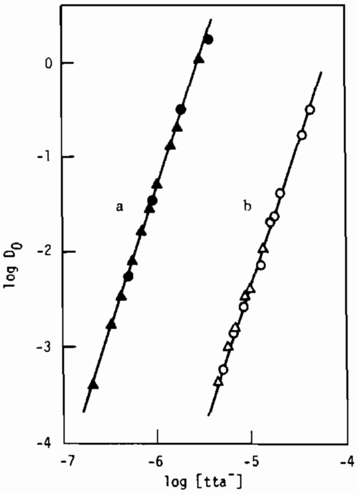

Fig. 1. Extraction of Tm(III) with Htta in benzene (a) and cyclohexane (b). $[Htta]_{init}$ = 1 × 10^{-2} M (▲, △), 1 × 10^{-3} M (●, ○).

ratio of Tm(III) against the logarithm of the equilibrium concentration of tta⁻ anion in the aqueous phase are shown in Fig. 1. The equilibrium concentration of tta⁻ in the aqueous phase was calculated as follows:

$$[A^-] = \frac{C_{HA}}{(P_{HA}+1)[H^+]/K_{HA}+1} \qquad (9)$$

where C_{HA} denotes the initial concentration of Htta. The literature values of K_{HA} and P_{HA} were adopted, *i.e.* log K_{HA} is −6.23 [11], and log P_{HA} is 1.62 [12] for benzene and 0.56 [13] for cyclohexane. The distribution ratios plotted against log[tta⁻] are independent of the initial concentration of Htta in both the organic solvent systems, and the plots give a straight line with a slope of 3.0, as is expected from the extraction of $Tm(tta)_3$. The extraction constant, K_{ex}, was calculated experimentally from the following relation:

$$K_{ex} = \left(\frac{K_{HA}}{P_{HA}}\right)^3 \frac{D_0}{[A^-]^3}$$

The values of log K_{ex} in both organic solvents are listed in Table II.

Synergic Extraction of Tm(III) with Htta and a Neutral Ligand

The synergic extraction of Tm(III) with Htta and 1 × 10^{-4} M phen in benzene and cyclohexane was carried out and the plots of log *D* against log [tta⁻] at a constant pH are shown in Fig. 2. The large synergic effect can be observed by comparing with the plots in Fig. 1. The straight lines with a slope of 3.0 are again clear in both solvent systems, and this suggests that the three molecules of tta⁻ are involved in the synergic extraction of Tm(III).

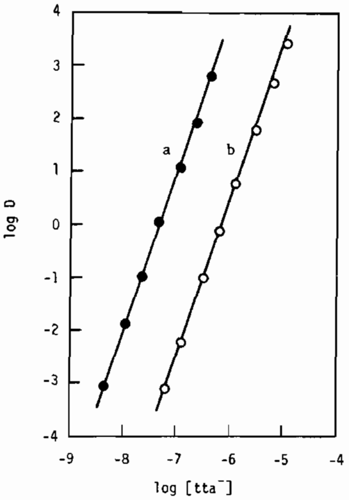

Fig. 2. Dependence on the concentration of Htta in Tm(III)–Htta–phen systems. $[phen]_{init}$ = 1 × 10^{-4} M, (a) benzene, pH 3.52, (b) cyclohexane, pH 3.97.

The plots of log D/D_0 against log $[\bar{S}]$ in the synergic extraction of Tm(III) with 1 × 10^{-3} M Htta and various neutral bidentate ligands in benzene and cyclohexane are shown in Fig. 3. The equilibrium concentration of each neutral ligand in the organic phase was calculated from the following equation:

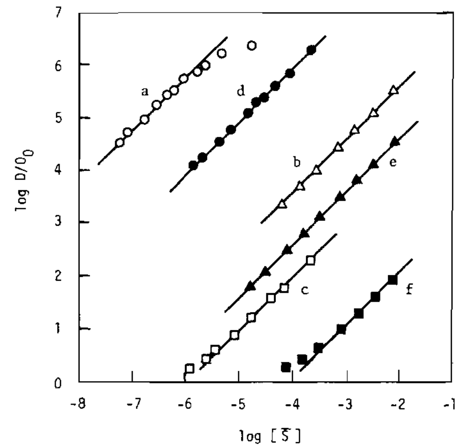

Fig. 3. Dependence of D/D_0 on the concentration of the neutral ligand in the organic phase. $[\text{Htta}]_{\text{init}} = 1 \times 10^{-3}$ M. Cyclohexane system: (a) phen, pH 3.8, (b) bpy, pH 4.0, (c) dmp, pH 5.0. Benzene system: (d) phen, pH 3.6, (e) bpy, pH 3.2, (f) dmp, pH 4.5.

$$[\bar{S}] = \frac{C_S}{1 + (1 + [H^+]/K_{HS})/P_S} \tag{11}$$

where C_S denotes the initial concentration of S. The acid dissociation constant, K_{HS}, of a protonated ligand and the partition coefficient, P_S, of the neutral ligand are known, as summarized in Table I. These plots give straight lines with a slope of unity, so that the chelate and the neutral bidentate ligand form only the 1:1 adduct. The deviation of the plots from the straight line observed in the higher phen concentration range in the phen-cyclohexane system seems to be attributed to an interaction between Htta and phen in the organic phase. Similar phenomena have been reported in the systems of some β-diketones and trioctylphosphine oxide [1].

It is concluded from these results that the extracted adduct of Tm(III) with Htta and neutral bidentate ligand is the only type of a mixed ligand complex as $\text{Tm(tta)}_3\text{S}$ for all the bidentate ligands, and no evidence for a formation of higher adduct as $\text{Tm(tta)}_3\text{S}_2$ is observed.

For comparison, the synergic extraction of Tm(III) with Htta and a unidentate ligand, py, is examined in Fig. 4. The value of log D/D_0 rises rapidly with increasing log [$\overline{\text{py}}$] and, in cyclohexane solvent, the plots in the higher concentration region of py are close to a straight line with a slope of two, so that the adduct formed finally is $\text{Tm(tta)}_3\text{(py)}_2$. In the benzene solvent system such a limiting slope cannot be clearly observed even at a higher concentration of py as 0.1 M, but it may be concluded that the adduct formed in this system is the same as the adduct in the cyclohexane system. An X-ray crystallographic study on a similar type of rare earth (III) β-diketonate adduct complex demonstrated that

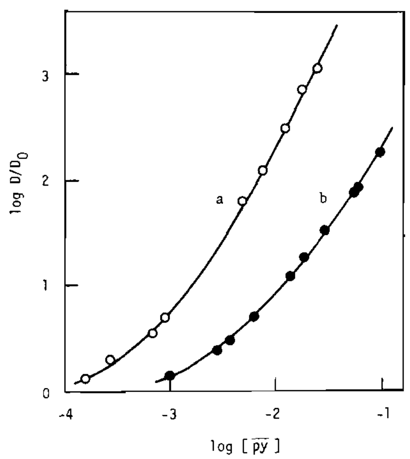

Fig. 4. Dependence of D/D_0 on the concentration of py in the organic phase. $[\text{Htta}]_{\text{init}} = 1 \times 10^{-3}$ M, (a) cyclohexane, (b) benzene.

$\text{Eu(dpm)}_3\text{(py)}_2$, where Hdpm denotes dipivaloylmethane, is the eight coordination complex with distorted square antiprismatic geometry [14].

The adduct formation constants, β_s, is the present synergic extraction systems are calculated from eqn. (6) using the least-squares fitting method, and are summarized in Table II. The values of the adduct formation constants for these bidentate amines are large and $\beta_{s,1}$ for bpy, which seems to be a quasi dimer type compound of py, is larger than $\beta_{s,2}$ for py. This suggests that bpy coordinates directly to the central metal of the chelate as a bidentate ligand. Thus the coordination number of Tm(III) in the adduct with the bidentate ligand seems to be eight. This may be supported by the X-ray crystallographic study on the similar mixed ligand compound, $\text{Nd(tta)}_3\text{bpy}$ [15]. In the synergic extraction, trioctylphosphine oxide is known as the most powerful unidentate ligand amoung commonly used neutral ligands, but $\beta_{s,1}$ for the present bidentate ligands (especially for phen) is very large, larger than $\beta_{s,2}$ in Htta – trioctylphosphine oxide – cyclohexane system (log $\beta_{s,2} = 11.32$) [16].

The values of $\beta_{s,1}$ for the bidentate ligands decrease in the following order; phen > bpy > dmp. The order of β_s values must be compared with the order of the basicity of neutral ligands. When we adopt the acid dissociation constant of the protonated ligand, pK_{HS}, as a simple measure of the basicity, that is dmp > phen > bpy, the smaller $\beta_{s,1}$ value for dmp than the $\beta_{s,1}$ value for bpy in the present case seems to be unusual. This may be attributed to the steric hindrance of two methyl groups near the nitrogen donor atoms of dmp. If so, the steric effect will be not so serious in the bivalent metal chelate compared with the tervalent metal chelate. In fact, in the synergic extraction of Mn(II) as $\text{Mn(tta)}_2\text{S}$ the order of $\beta_{s,1}$ is phen > dmp >

bpy [6]. Thus the steric effect may be closely related to the structure of the chelate, *e.g.*, steric crowding around the central metal atom.

Little is known on the organic solvent effect in the synergic extraction with a bidentate ligand. From the results in all the systems listed in Table II, it is obvious that the values of β_s in cyclohexane are larger than those in benzene. This result is in good agreement with that in the Tm(III)–Hacac–phen system [17]. It was reported that in the synergic extraction of Eu(III) with Htta and phen or bpy, the values of $\beta_{s,1}$ for cyclohexane are smaller than those for benzene [10]. This is not a plausible result, which may be responsible partly to the different value of the partition coefficients for the neutral ligands, that is, $\log P_S = 0.11$ [10] is different from the present value of -0.97 in the phen–cyclohexane system. The solvent (diluent) effect in the synergic extraction has been thoroughly discussed by the aid of the regular solution theory, and these studies verify a favorable role of cyclohexane as a solvent in the synergism [17–19].

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