Synergic Extraction Equilibrium of Mn(II) with 4,4,4-Trifluoro-1-(2-thienyl)-1,3-butanedione and Neutral Multidentate Ligands, Such as Terpyridine and Tetraphenyldiphosphane Dioxide

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The extraction equilibrium of Mn(II) was clarified in novel synergic extraction systems using 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (Htta) and neutral multidentate ligands, such as 2,2′:6′,2″-terpyridine (terpy) and tetraphenyldiphosphane dioxide (tpdpo), into benzene. No oxidation of Mn(II) and large synergic effect were observed both in the Htta–terpy and Htta–tpdpo systems, and quantitative extraction of Mn(II) was done, which was not attained with Htta only. Mn(II) was extracted as $\mathrm{Mn(tta)_2(terpy)}$ in the Htta–terpy system, where only two nitrogen atoms of terpy would coordinate to Mn. In the Htta–tpdpo system, two species, i.e. $\mathrm{Mn(tta)_2(tpdpo)}$ and $\mathrm{Mn(tta)_2(tpdpo)_2}$, formed in the benzene phase, where tpdpo functioned as a unidentate ligand. The adduct formation constants (β_s) and the synergic extraction constants ($K_\mathrm{ex,s}$) were obtained and compared with those of other related compounds.

Manganese is one of the elements that exist widely in biological and geological environment. Mn^{2+} has less extractability[1)] among the first transition series, and its quantitative extraction can not often be attained with only a bidentate acidic chelating agent. Mn(II) tends to have two molecules of auxiliary ligand in a crystal with acidic chelating agents.[2,3)] Therefore, the extracted species of Mn(II) would contain two molecules of water and its hydrophobicity would not be very high. For an extracted metal ion the coordination number of which was not saturated with chelating agents only, the synergic extraction using a neutral ligand was frequently adopted to increase extractability.

For the synergic extraction of Mn(II), tributyl phosphate (tbp),[4)] trioctylphosphane oxide (topo)[4,5)] or pyridine derivatives[6,7)] have been used as unidentate ligands, and 1,10-phenanthroline or 2,2′-bipyridine (bpy) was examined as bidentate ligands.[4,7,8)] The adduct formation constants of these bidentate ligands are larger than that of unidentate ligand of similar structure, and extractability was improved. A neutral ligand having a coordination site of more than two is expected to show a further large synergic effect, but no report on such a ligand has appeared.

A large number of reports include the synergic extraction using oxygen-containing unidentate ligands, such as tbp or topo, for various elements. Umetani et al. recently reported about the large synergic effect of oxygen-containing bidentate ligands,[9,10)] but these compounds were applied in limited extraction systems.

We reported that 2,2′:6′,2″-terpyridine (terpy)[11)] and tetraphenyldiphosphane dioxide (tpdpo)[12)] showed large synergic effects in the extraction of lanthanoids(III). In this study, the equilibrium of synergic extraction of Mn(II) using terpy or tpdpo is characterized in combination with the geometry of Mn(II).

Experimental

Materials. 4,4,4-Trifluoro-1-(2-thienyl)-1,3-butanedione (2-thenoyltrifluoroacetone, Htta) and 2,2′:6′,2″-terpyridine (terpy) were purchased and purified by vacuum sublimation.[11)] Tetraphenyldiphosphane dioxide (tpdpo) was synthesized and identified as before.[12)] Benzene was stirred with concd $\mathrm{H_2SO_4}$ and distilled over $\mathrm{CaH_2}$. Water was double-distilled and deionized. Other reagents were of analytical reagent grade.

A radioisotope $^{54}\mathrm{Mn}$, used as a tracer, was purchased from New England Nuclear Co. A radioactive solution of Mn(II) was prepared by adding the radioisotope to a sample of a standard solution of Mn(II), evaporating to dryness, and redissolving the residue in a 1×10^{-3} M (1 M=1 mol dm^{-3}) HCl solution containing 0.25 M ascorbic acid.

Procedure. An aqueous solution (5 cm^3) containing 1×10^{-6}—1×10^{-5} M Mn(II) labeled with its radioisotope $^{54}\mathrm{Mn}$ and 1×10^{-4}—1×10^{-3} M ascorbic acid was placed in a 20 cm^3 centrifuging tube. The pH of the aqueous phase was adjusted to 6—7 with 1×10^{-2} M of 2-(*N*-morpholino)ethanesulfonic acid (pK_a 6.15) and sodium hydroxide solutions. The ionic strength was fixed at 0.1 with sodium perchlorate. A benzene solution (5 cm^3) containing 1×10^{-4}—3×10^{-3} M Htta and 8×10^{-6}—1×10^{-2} M terpy or tpdpo was added to the aqueous solution and shaken for 15 min—3 h. After centrifugation for phase separation, a sample (3 cm^3) of each phase was pipetted and γ-activity was measured with an NaI(Tl) well-type scintillation counter. The distribution ratio of Mn(II) was obtained as the γ-activity ratio. The equilibrium pH of the aqueous phase was measured with a glass electrode immediately after the phase separation.

From the organic phase separated after the first extraction, Mn(II) was back-extracted into a fresh aqueous phase whose pH and ionic strength were adjusted to 6—7 and 0.1, respectively (containing no ascorbic acid). The distribution ratio of Mn(II) was calculated as mentioned above.

All procedures were done in a thermostatted room at 25±1 °C.

Theoretical

The distribution ratio (D_o) of a divalent metal ion (M^{2+}) with a chelating extractant (HA) can be expressed as:

$$D_\mathrm{o}=\frac{[\overline{\mathrm{MA}_2}]}{[\mathrm{M}^{2+}]+\sum\limits_m[\mathrm{MA}_m^{(2-m)+}]}=\frac{K_\mathrm{ex}P_\mathrm{HA}^2[\mathrm{A}^-]^2}{K_\mathrm{HA}^2(1+\sum\limits_m\beta_{\mathrm{A},m}[\mathrm{A}^-]^m)},\tag{1}$$

where K_HA and P_HA are the acid-dissociation constant and partition coefficient of HA, respectively, and the upper-bar denotes the organic phase. $\beta_{\mathrm{A},m}$ is the formation constant of $\mathrm{MA}_m^{(2-m)+}$ and A^- the acid-dissociated anion of HA in the aqueous phase. K_ex denotes the extraction constant for the following equilibrium:

$$\mathrm{M}^{2+}+2\overline{\mathrm{HA}}\rightleftharpoons\overline{\mathrm{MA}_2}+2\mathrm{H}^+.\tag{2}$$

In the region where the concentration of A^- is very low, the $\sum\limits_m\beta_{\mathrm{A},m}[\mathrm{A}^-]^m$ term is negligibly small in Eq. 1, hence D_o is proportional to the second power of $[\mathrm{A}^-]$.

In the synergic extraction of M^{2+} with HA and a neutral ligand (S), the distribution ratio (D) can be expressed as:

$$D=\frac{[\overline{\mathrm{MA}_2}]+\sum\limits_n[\overline{\mathrm{MA}_2\mathrm{S}_n}]}{[\mathrm{M}^{2+}]+\sum\limits_m[\mathrm{MA}_m^{(2-m)+}]}=\frac{K_\mathrm{ex}P_\mathrm{HA}^2[\mathrm{A}^-]^2(1+\sum\limits_n\beta_{\mathrm{s},n}[\overline{\mathrm{S}}]^n)}{K_\mathrm{HA}^2(1+\sum\limits_m\beta_{\mathrm{A},m}[\mathrm{A}^-]^m)},\tag{3}$$

where $\beta_{\mathrm{s},n}$ is the adduct formation constant in the organic phase corresponding to the formation constant of the following equilibrium:

$$\overline{\mathrm{MA}_2}+n\overline{\mathrm{S}}\rightleftharpoons\overline{\mathrm{MA}_2\mathrm{S}_n}.\tag{4}$$

The next simple equation is obtained from Eqs. 1 and 3:

$$D/D_\mathrm{o}=1+\sum_n\beta_{\mathrm{s},n}[\overline{\mathrm{S}}]^n.\tag{5}$$

If $\mathrm{MA}_2\mathrm{S}_n$ is the dominant species in the organic phase, D/D_o will be proportional to the n-th power of $[\overline{\mathrm{S}}]$. The synergic extraction constant ($K_{\mathrm{ex,s},n}$) for the following equilibrium:

$$\mathrm{M}^{2+}+2\overline{\mathrm{MA}}+n\overline{\mathrm{S}}\rightleftharpoons\overline{\mathrm{MA}_2\mathrm{S}_n}+2\mathrm{H}^+,\tag{6}$$

can be calculated from the simple relationship as

$$K_{\mathrm{ex,s},n}=K_\mathrm{ex}\cdot\beta_{\mathrm{s},n}.\tag{7}$$

Results and Discussion

Extraction of Mn(II) with Htta. To obtain enough shaking time to attain the extraction equilibrium, the organic phase containing 1.05×10^{-2} M Htta and the aqueous phase whose pH was fixed at 6.4 were shaken for 10 min—3 h. The distribution ratio of Mn(II) was constant ($\log D_\mathrm{o}$ -1.26 ± 0.03) in this time range, and thus the extraction equilibrium was reached rapidly. The shaking time was fixed at 1 h in subsequent experiments.

The extraction of Mn(II) was done with various Htta concentrations in benzene and the plots of $\log D_\mathrm{o}$ against $\log[\mathrm{tta}^-]$ are shown in Fig. 1. The equilibrium concentration of tta^- in the aqueous phase was calculated as:

$$[\mathrm{tta}^-]=\frac{C_\mathrm{HA}}{(P_\mathrm{HA}+1)[\mathrm{H}^+]/K_\mathrm{HA}+1},\tag{8}$$

where C_HA denotes the initial concentration of Htta in the organic phase. The literature values of K_HA and P_HA were adopted, i.e., pK_HA, 6.23[13] and $\log P_\mathrm{HA}$, 1.62.[14] The plots show linear relationship with a slope of 2.0. This indicates that two molecules of tta^- participate in the extraction of Mn(II) according to Eq. 1. It was sometimes reported that Mn(II) was oxidized during the extraction,[4,15] but the oxidation of Mn(II)

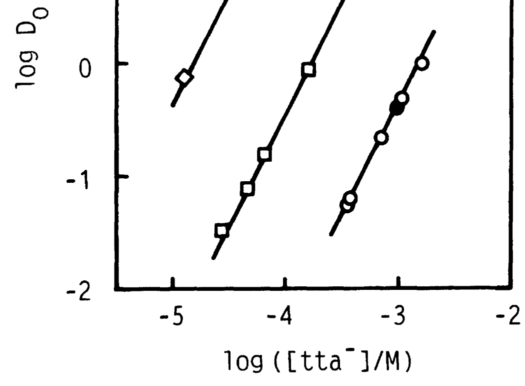

Fig. 1. Dependence of D_o or D of Mn(II) on the concentration of tta^- in the Htta (○, ●), Htta–terpy (◇, ◆), and Htta–tpdpo systems (□). Htta, 1.3×10^{-4}—2.8×10^{-2}M; terpy, 1.1×10^{-3}M; tpdpo, 1.0×10^{-3}M; pH 6.5—6.9. Open symbols, forward extraction in the presence of 1.0×10^{-3} M ascorbic acid. Blackened symbols, back-extraction in the absence of ascorbic acid.

is negligible in this case. This is also supported by the fact that plots for the back-extraction (without ascorbic acid) are located on this line.

K_{ex} is calculated with Eq. 1 as $10^{-10.06}$, which agrees well with the literature value, $10^{-10.07}$.4) K_{ex} is very small, therefore quantitative extraction was not attained with Htta only (cf. Fig. 1).

Synergic Extraction of Mn(II) in the Htta–terpy or Htta–tpdpo system. The synergic extraction of Mn(II) was done with various concentrations of Htta, terpy or tpdpo. To prevent Mn(II) from oxidizing, ascorbic acid was added in the synergic extraction systems.

The plots of $\log D$ against $\log[\mathrm{tta}^-]$ are shown in Fig. 1. A large synergic effect is observed as compared with Htta only, that is, D is 10000 or 100 times larger. In the presence of terpy or tpdpo, the plots also gave linear relationships with slopes of 2.0 and 1.9 for the Htta–terpy and Htta–tpdpo system, respectively. Therefore it proved that two molecules of tta^- participate in the synergic extraction of Mn(II). Plots of the back-extraction agreed with those of the forward extraction, and this indicates that the oxidation state of Mn was kept to divalent.

The plots of $\log(D/D_o)$ against $\log[\overline{S}]$ are shown in Fig. 2, where the D_o value was calculated with Eq. 1 using the K_{ex} value. We had made sure that the equilibrium concentration of terpy or tpdpo in the benzene phase, $[\overline{S}]$, was equal to the initial concentration in these pH ranges.11,12) The slope of the plots in the Htta–terpy system is 1.0, which implies that the dominant extracted species is $\mathrm{Mn(tta)_2(terpy)}$. The $\beta_{s,1}$ was calculated from Eq. 5 and listed in Table 1. In the Htta–tpdpo system, the plots in a higher concentration range of tpdpo deviate positively from a straight line with a slope of 1.0. This indicates that adducts, $\mathrm{Mn(tta)_2(tpdpo)}$ and $\mathrm{Mn(tta)_2(tpdpo)_2}$, form in the organic phase. The adduct formation constants, $\beta_{s,1}$ and $\beta_{s,2}$, calculated with Eq. 5 by the non-linear least-squares method, are summarized in Table 1. The line for the Htta–tpdpo system in Fig. 2, which is drawn with Eq. 5 using $\beta_{s,1}$ and $\beta_{s,2}$ values, accords with observed values.

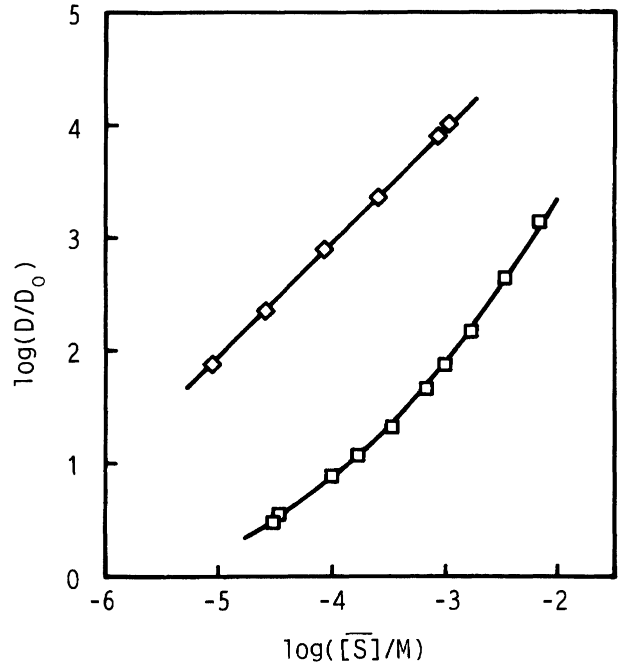

Fig. 2. Dependence of D/D_o on the concentration of neutral ligand in the benzene phase, $[\overline{S}]$. ◇ terpy, □ tpdpo.

Some reports included the association of a chelating agent and a neutral ligand in the organic phase.16,17) If the association is not negligible, the plots in Fig. 1 would be located lower than the line of slope 2 at a higher concentration range of Htta. However this was not observed, so the association doesn't need to be taken into consideration for these concentration ranges. The situation agrees with those in the extraction of lanthanoids(III).11,12)

The Adduct Formation Constant and the Coordination Number of Manganese(II). Terpy has three nitrogen atoms for coordination to a metal ion. In fact, it was suggested that terpy functioned as a tridentate ligand for light lanthanoids in the organic phase.11) Three nitrogens of terpy coordinate fully to a europium(III) β-diketonato complex in a crystal state.18) The $\beta_{s,1}$ value of Mn for terpy ($\log\beta_{s,1}$ 6.96) is smaller than that for bidentate ligand, bpy ($\log\beta_{s,1}$ 8.00),4) the basicity of which is nearly equal to terpy.11) This indicates that only two nitrogen atoms of terpy coordinate to Mn and that a remaining free pyridyl-group causes either steric hindrance or an increment of the activity of the extracted complex. (The latter influence of the free pyridyl group would be brought on by exposure of the polar N-atom of this group to the non-polar phase.) Similar discussions are available for lanthanoids(III):11,19) La has a large ionic radius, and thus terpy coordinates as a tridentate ligand, and the $\beta_{s,1}$ value for terpy is larger than that for bpy ($\log\beta_{s,1}$ 7.16 for terpy,11) 5.36 for bpy19)). The ionic radius of Lu is smaller than La, and thus terpy functions in a manner similar to Mn(II) and the $\beta_{s,1}$ of Lu for terpy is smaller than that for bpy ($\log\beta_{s,1}$ 4.75 for terpy,11) 6.51 for bpy19)). The coordination number of Mn(II) is sometimes more than six.20—22) In this study, this phe-

Table 1. Equilibrium Constants of the Synergic Extraction of Mn(II) with Htta and Neutral Multidentate Ligand (S)

S	$\log\beta_{s,1}$	$\log\beta_{s,2}$	$\log K_{ex}$	$\log K_{ex,s,1}$	$\log K_{ex,s,2}$
terpy	6.96	—a)	−10.06	−3.10	—a)
tpdpo	4.78	7.27	−10.06	−5.28	−2.79

a) Not observed.

nomenon was expected, but the coordination number of Mn(II) would be normally six (i.e., octahedral) as mentioned above. In other words, the four coordination sites of Mn(II)are filled with two molecules of tta^- and the other two sites are occupied with terpy, which functions as a bidentate ligand.

It was expected that tpdpo functioned as a bidentate ligand with two phosphoryl-groups and formed a stable five-membered ring, and consequently had a large synergic effect. However, it was observed that the synergic effect of tpdpo was smaller than that of terpy and two molecules of tpdpo coordinate not only to Mn(II) but also to lanthanoids(III).12) If two oxygen atoms of tpdpo function fully, the coordination number of Mn is eight. This cannot be realized. Since the two oxygen atoms of tpdpo are in the *trans*-position in a crystal state,23) this compound would function as a monodentate ligand in this synergic extraction system.

To compare these with other compounds, tbp and topo are taken, which are unidentate ligands and have the same functional group, P=O, as tpdpo. As the $\beta_{s,2}$ values of Mn(II) in benzene, $10^{6.90}$ and $10^{10.25}$ were obtained in the Htta–tbp and Htta–topo systems, respectively.4) Although the donor number has been used as an index for the coordination power, the donor number of tpdpo is not available. Therefore, another parameter was adopted in this study. For pentavalent organo-phosphorus compounds, it has been reported that a substitute with large electro-negativity made the P=O bond strong and the electron density or donicity of oxygen atom decreased.24,25) The stretching vibrations of P=O, ν(P=O), of tbp and topo were measured as 1283 and 1160 cm^{-1}, respectively by IR measurement.25) The lower frequency for topo indicates that the donicity of the oxygen atom of topo is higher, and this agrees with the common results of the synergic extraction: topo has a larger synergic effect than tbp. Since ν_{as}(P=O) and ν_s(P=O) of tpdpo was reported as 1176 and 1182 cm^{-1} respectively,23) the donicity order of the oxygen atom is thought to be topo>tpdpo>tbp. The order of $\beta_{s,2}$ of Mn(II) agrees with this order, so the magnitude of $\beta_{s,2}$ is thought to be mainly controlled by the donicity of the oxygen atom of ligand.

The extraction equilibrium of Mn(II) was clarified in a novel synergic extraction system, i.e., the Htta–terpy and Htta–tpdpo systems. Mn(II) was extracted into benzene as $Mn(tta)_2(terpy)$ in the former. On the other hand, $Mn(tta)_2(tpdpo)$ and $Mn(tta)_2(tpdpo)_2$ formed in the benzene phase in the latter. Large synergic effects observed in both systems allowed the quantitative extraction of Mn(II), which was hard to attain with Htta only.

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