

Extraction Equilibrium Constants of Scandium(III) and Yttrium(III) in Acetylacetonate–Organic Solvent Systems and some Comparisons with Rare Earths(III)

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Abstract

The extraction equilibria of scandium(III) and yttrium(III) with acetylacetonate into various organic solvents have been investigated at 25 °C. The liquid–liquid partition coefficients and the formation constants of these chelates have been determined and compared with those of lanthanoid(III) chelates. The effect of organic solvents on the partition coefficient is quantitatively explained with the aid of the regular solution theory. A clear correlation between the partition coefficient and the successive formation constants of these acetylacetonate chelates is demonstrated.

Introduction

Solvent extraction is one of the powerful separation methods and has been widely used in applied fields of science such as hydrometallurgy of rare metals and reprocessing of nuclear fuel. The most important process governing the chelate extraction efficiency of metal ions is considered to be the formation of extractable metal chelates in an aqueous phase and its liquid–liquid partition. In our recent investigations [1, 2], it was demonstrated that the liquid–liquid partition coefficient of metal chelates is primarily governed by the formation energy of a cavity of suitable size to accommodate the solute in each phase and the specific interactions among solute and solvent molecules. Additionally, it has been elucidated that the solute–solvent interaction is strongly dependent on the nature of the chemical bonding between the central metal and the chelating ligand [2, 3].

In the present paper, the extraction equilibrium of scandium(III) and yttrium(III) has been investigated using acetylacetonate and several organic solvents, including 1-octanol, the partition coefficients and the

formation constants being determined. The solvent effect on the partition coefficient is elucidated with the aid of the regular solution theory. The partition coefficients and the formation constants of the scandium(III) and yttrium(III) chelates are compared with those of the lanthanoids(III) reported previously [4] and the correlation among these equilibrium constants is discussed.

Experimental

Materials and Apparatus

A radioisotope, ^{46}Sc , was produced by neutron irradiation of scandium oxide (99.9% purity) in the nuclear reactor (JRR-2) of the Japan Atomic Energy Research Institute at a thermal neutron flux of $3 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ for 12 d. The irradiated oxide was dissolved in hydrochloric acid, evaporated to dryness, and redissolved in 0.01 M perchloric acid. A radioisotope, ^{88}Y , was produced by the (p,n) reaction of ^{88}Sr by bombarding strontium oxide (99% purity) with 18 MeV protons at 2 μA for 2 h using a cyclotron of Tohoku University. The irradiated target was dissolved in dilute hydrochloric acid. The pH value of the solution was adjusted to about 5 with 0.1 M acetate buffer and sodium hydroxide solution and washed with 0.1 M 8-quinolinol in benzene to remove metal impurities involved in the strontium oxide target. After washing the aqueous phase with benzene solvent, carrier-free ^{88}Y was extracted with 0.02 M thenoyltrifluoroacetone into benzene. After washing the organic phase with an aqueous solution (pH 5), ^{88}Y was back-extracted with 10^{-4} M hydrochloric acid and washed with benzene several times. The ^{88}Y solution obtained was treated with nitric acid, evaporated to dryness, and redissolved in 0.01 M perchloric acid. The radiochemical purity of the ^{46}Sc and ^{88}Y solution was checked by γ -ray spectrometry. Radioactive scandium(III) and yttrium(III) perchlorate solutions of the desired concentrations were prepared by mixing each radioisotope solution with the standard carrier solution (0.02 M) prepared from the high purity oxide.

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Acetylacetone (Hacac) and the organic solvents used were purified as described in previous papers [4, 5]. Unless otherwise stated, the reagents used were of guaranteed reagent grade.

The apparatus used were the same as those used previously [4, 5].

Extraction Procedure for Metal(III)

An aqueous solution (5 ml) containing 1×10^{-6} – 1×10^{-5} M scandium(III) or 7×10^{-6} – 8×10^{-4} M yttrium(III), labelled with ^{46}Sc or ^{88}Y , respectively, was placed in a 30-ml extraction vial with a ground glass stopper. An organic solution (5 ml) containing 0.03–0.1 M Hacac was added, shaken for 0.5–2 h at 25 °C, and centrifuged. An aliquot was taken from each phase and the γ -activity was measured. The distribution ratio (D) of the metal(III) was calculated as the ratio of the counting rates for both phases. The pH value of the aqueous phase was adjusted with 0.1 M perchloric acid, 0.001 M acetic acid, and 0.001–0.1 M sodium hydroxide solutions. The equilibrium pH value was measured immediately after shaking. The ionic strength of the aqueous phase was maintained at 0.10 M with sodium perchlorate.

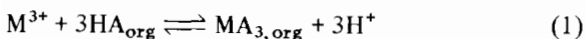
Attainment of the extraction equilibrium was always confirmed by agreement between the distribution ratios of the metal(III) in forward and backward extraction.

Determination of the Partition Coefficient of Hacac into 1-Octanol

A 1-octanol solution containing 4×10^{-5} M Hacac was pre-equilibrated with a 0.10 M perchlorate solution at pH 3 and then the absorbance of the organic phase (A_0) was measured at 274 nm. A portion (5 ml) of the organic phase was shaken with a 0.10 M perchlorate solution (5 ml) of pH 3 for 0.5–2 h at 25 °C and the absorbance of the organic phase (A_1) was measured at 274 nm. The partition coefficient of Hacac between 1-octanol and the aqueous phase was calculated as $P_{\text{HA}} = A_1/(A_0 - A_1)$.

Results and Discussion

The extraction equilibrium of a trivalent metal, M^{3+} , with an acidic chelating agent, HA, can be expressed as follows



$$K_{\text{ex}} = \frac{[\text{MA}_3]_{\text{org}} [\text{H}^+]^3}{[\text{M}^{3+}] [\text{HA}]_{\text{org}}^3} \quad (2)$$

where the subscript org denotes the organic phase and K_{ex} the extraction constant. The distribution ratio of the metal(III) is written by

$$D = \frac{[\text{MA}_3]_{\text{org}}}{[\text{M}^{3+}] + \Sigma [\text{MA}_n^{(3-n)+}]} \quad (3)$$

Equation 3 can be rewritten by using the partition coefficient of the neutral chelate MA_3 , P_{M} , the overall formation constant of $\text{MA}_n^{(3-n)+}$ in the aqueous phase, β_n

$$D = \frac{P_{\text{M}} \beta_3 [\text{A}^-]^3}{1 + \Sigma \beta_n [\text{A}^-]^n} \quad (4)$$

and further using K_{ex}

$$D = K_{\text{ex}} \left(\frac{P_{\text{HA}}}{K_{\text{HA}}} \right)^3 \frac{[\text{A}^-]^3}{1 + \Sigma \beta_n [\text{A}^-]^n} \quad (5)$$

where P_{HA} and K_{HA} denote the partition coefficient and the acid dissociation constant of HA.

The extraction of scandium(III) with 0.1 M Hacac in various organic solvents was carried out and the plots of the logarithms of the distribution ratios against the logarithms of the acetylacetonate (acac) concentrations in the aqueous phase are given in Fig. 1. The acac concentration was calculated as

$$[\text{A}^-] = \frac{C_{\text{HA}}}{1 + (P_{\text{HA}} + 1)[\text{H}^+]/K_{\text{HA}}} \quad (6)$$

where C_{HA} is the initial concentration of Hacac. The logarithmic value of P_{HA} for 1-octanol was determined to be 0.013, and the literature values for other solvents were adopted, i.e., –0.052 for heptane [6], 0.503 for carbon tetrachloride [7], 0.736 for benzene [7], and 1.367 for chloroform [7]. The logarithmic

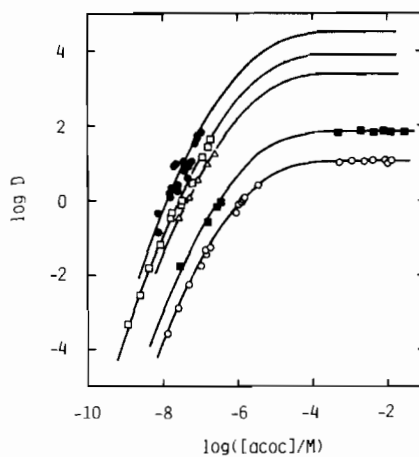


Fig. 1. Distribution ratio of scandium(III) as a function of acac concentration in an aqueous phase. $[\text{Hacac}]_{\text{init}} = 0.1$ M, $[\text{Sc(III)}]_{\text{init}} = 1 \times 10^{-6}$ – 1×10^{-5} M, pH = 1.7–8.2. \circ , heptane; \triangle , carbon tetrachloride; \square , benzene; \bullet , chloroform; \blacksquare , 1-octanol.

TABLE I. Partition Coefficients and Extraction Constants of Scandium(III) and Yttrium(III) Acetylacetonate Chelates at 25 °C

Number ^a	Solvent	Sc(acac) ₃		Y(acac) ₃	
		log P _M	log K _{ex}	log P _M	log K _{ex}
1	Heptane	1.041	-5.87	-4.459	-17.03
2	Carbon tetrachloride	3.372	-5.21	-1.809	-16.05
3	Benzene	3.891	-5.39	-1.439	-16.38
4	Chloroform	4.499	-6.67	-0.531	-17.36
5	1-Octanol	1.835	-5.27	0.498	-12.27

^aSee Figs. 3 and 4.

value of K_{HA} was adopted as -8.82 [8]. In the typical solvent systems of heptane and 1-octanol, the distribution ratio increases with an increase in the acetylacetonate concentration and reaches a limiting value in the high concentration region of acetylacetonate. This suggests a stepwise formation of the chelates, $Sc(acac)^{2+}$, $Sc(acac)_2^+$, $Sc(acac)_3$, in the aqueous phase, and therefore eqn. (4) can be rewritten using the successive formation constants, K_n ($n = 1-3$),

$$\log D = \log P_M - \log \left(\frac{1}{K_1 K_2 K_3 [A^-]^3} + \frac{1}{K_2 K_3 [A^-]^2} + \frac{1}{K_3 [A^-]} + 1 \right) \quad (7)$$

The partition coefficients of scandium(III) chelate in the heptane or the 1-octanol system can directly be determined as the limiting values of the distribution ratios. The formation constants were determined by the least-squares fitting (computer program SALS, University of Tokyo) of the distribution data in the heptane system according to eqn. (7). Then the partition coefficients in other solvent systems, where a plateau region of $\log D$ cannot be measured experimentally, were determined by the least-squares fitting using K_1 , K_2 , and K_3 obtained in the heptane system. The extraction constants were calculated as $K_{ex} = P_M \beta_3 K_{HA}^3 P_{HA}^{-3}$. These equilibrium constants are listed in Tables I and II. The solid lines in Fig. 1 are drawn based on the computed values using these equilibrium constants and are in good agreement with the experimental plots.

The extraction of yttrium(III) with 0.03–0.1 M Hacac in various organic solvents was carried out and the plots for $\log D$ versus $\log [acac]$ are given in Fig. 2. The plots for each solvent give a curve with a maximum corresponding to the stepwise formation of the yttrium(III) chelates such as $Y(acac)^{2+}$, $Y(acac)_2^+$, $Y(acac)_3$, and $Y(acac)_4^-$. In Fig. 2, the distribution ratios plotted against acetylacetonate concentrations, which are adjusted by various combinations of differ-

TABLE II. Successive Formation Constants of Scandium(III) and Yttrium(III) Acetylacetonate Chelates at 25 °C

Metal(III)	log K ₁	log K ₂	log K ₃	log K ₄
Sc(III)	8.02	6.36	5.01	—
Y(III)	(5.87) ^a	4.77	3.09	1.74

^aLiterature value [9].

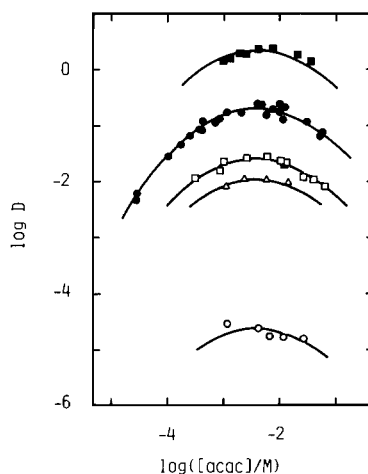


Fig. 2. Distribution ratio of yttrium(III) as a function of acac concentration in an aqueous phase. $[Hacac]_{init} = 0.03-0.1$ M, $[Y(III)]_{init} = 7 \times 10^{-6}-8 \times 10^{-4}$ M, pH = 6.6–10.4. \circ , heptane; \triangle , carbon tetrachloride; \square , benzene; \bullet , chloroform; \blacksquare , 1-octanol.

ent initial concentrations of acetylacetonate and different hydrogen ion concentrations, give reproducible results, and this shows that a lowering of the distribution ratio in the higher concentration region of acetylacetonate cannot be attributed to the hydrolysis of yttrium(III) but to formation of $Y(acac)_4^-$. The formation of such a higher complex was confirmed by the ion-pair extraction with tetraphenylarsonium in $Tm(III)-Hacac$ -chloroform systems [5]. Therefore, eqn. (4) is rewritten as follows

$$\log D = \log P_M - \log K_4 - \log [A^-]$$

$$- \log \left(\frac{1}{K_1 K_2 K_3 K_4 [A^-]^4} + \frac{1}{K_2 K_3 K_4 [A^-]^3} + \frac{1}{K_3 K_4 [A^-]^2} + \frac{1}{K_4 [A^-]} + 1 \right) \quad (8)$$

The values of P_M and K_n ($n = 1-4$) in the chloroform system were computed by the least-squares fitting based on this equation. Then the P_M values for other solvents were computed using the K_n values thus determined. A reliable value of K_1 was not obtained by the present technique because of the presence of only a small fraction of Y^{3+} and $Y(acac)^{2+}$ under the present experimental concentration range of acetylacetonate. The extraction constants were calculated as $K_{ex} = P_M \beta_3 K_{HA}^3 P_{HA}^{-3}$. These equilibrium constants are listed in Tables I and II. The solid lines in Fig. 2 indicate the computed values using these equilibrium constants and are in good agreement with the experimental plots.

The values of $\log K_{ex}$ for the scandium(III) chelate are much larger than those for the yttrium(III) chelate in all solvent systems. It is obvious that the difference in K_{ex} can be attributed to the difference not only in the formation constant but also in the partition coefficient. The value of $\log K_{ex}$ for the scandium(III) chelate lies between -5.21 and -6.67 in all solvent systems in spite of fairly large differences in $\log P_M$ in different solvents, *i.e.*, from 1.04 for heptane to 4.50 for chloroform. The same is almost true for the yttrium(III) chelate except with the 1-octanol system where K_{ex} is remarkably higher than those in other nonpolar organic solvents. This small solvent effect on K_{ex} is explained by a compensation between the partition coefficient of the chelate and that of the chelating agent. The following simple but important relation is found [1, 2, 10, 11],

$$\log P_M = \frac{V_M}{V_{HA}} \log P_{HA} + \text{constant} \quad (9)$$

where V denotes the molar volume, and the molar volume ratio V_M/V_{HA} is about three in the tris chelate. Figure 3 shows the correlation of P_M against P_{HA} in scandium(III) and yttrium(III) chelates. Plots for nonpolar solvents lie close to the straight line with a slope of 3. Hence, the value of $P_M P_{HA}^{-3}$ does not greatly vary with different nonpolar organic solvents. A quite large deviation for the 1-octanol system with yttrium(III) chelate is observed. A specific solute-solvent interaction in this system may be responsible.

The partition coefficient expressed by the molar fraction scale can be written as follows [1]

$$\ln P_s^o = \frac{V_s}{RT} [C_{ww} - C_{oo} + 2(C_{os} - C'_{ws})] \quad (10)$$

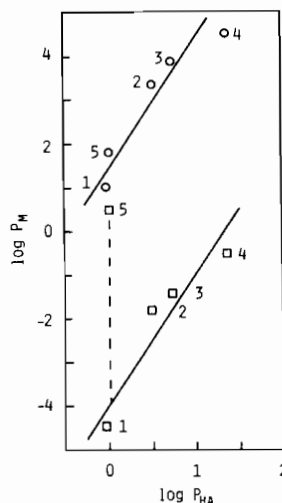


Fig. 3. Correlation between the partition coefficients of acetylacetonate and its scandium(III) or yttrium(III) chelate. The numbers correspond to those in Table I. \circ , $Sc(acac)_3$; \square , $Y(acac)_3$.

where V and C are the molar volume and the cohesive energy density, respectively. The subscripts s , w , and o denote the solute, water, and organic solvent, respectively. The parameter C'_{ws} involves any additional interaction between solute and water. When a geometric mean approximation is introduced for C_{os} and replaced with the solubility parameters, δ , eqn. (10) can be rewritten as

$$\frac{RT}{V_s} \ln P_s^o + C_{oo} = 2\delta_s \delta_o + C_{ww} - 2C'_{ws} \quad (11)$$

A linear relationship between the left-hand side of eqn. (11) and δ_o can be expected, and the apparent solubility parameter of the solute (δ_s) and an interaction term with water ($C_{ww} - 2C'_{ws}$) can be obtained from the slope and the intercept, respectively. The value of V_s of the chelate was assumed to be equal to the molar volume of the solid chelate, which is calculated from its density as given in the literature: $272 \text{ cm}^3 \text{ mol}^{-1}$ for the scandium(III) chelate [12] and $274 \text{ cm}^3 \text{ mol}^{-1}$ for the yttrium(III) chelate (monohydrate) [13]. Even if the molar volume of trihydrate of the yttrium(III) chelate ($303 \text{ cm}^3 \text{ mol}^{-1}$) [13] is used to calculate δ_s and $C_{ww} - 2C'_{ws}$, it has an influence on these calculated values of less than 5%. Figure 4 shows the plots for the scandium(III) and yttrium(III) chelates and gives a good linear relationship for each chelate in heptane, carbon tetrachloride, benzene and chloroform, but not in 1-octanol. The plot for 1-octanol in the scandium(III) system is slightly lower than the straight line expected from the plot for nonpolar solvents. This peculiar deviation cannot be explained in detail but may show a limitation of the regular solution concept

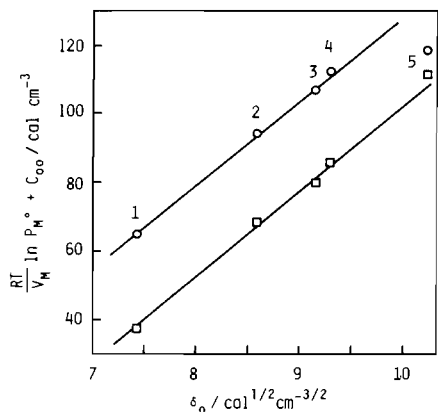


Fig. 4. Evaluation of the partition coefficients based on the regular solution theory. The numbers correspond to those in Table I. \circ , $\text{Sc}(\text{acac})_3$; \square , $\text{Y}(\text{acac})_3$.

when applied to an alcoholic solvent with a specific interaction among solvent molecules. The apparent solubility parameters of the scandium(III) and yttrium(III) chelates were nearly equal to each other and were calculated to be 12.42 and 12.85 $\text{cal}^{1/2} \text{cm}^{-3/2}$, respectively, from the slope of plots for four solvents. On the other hand, though we cannot give a strict physical explanation, the apparent interaction parameter, $C_{ww} - 2C'_{ws}$, obtained from the intercept of the straight line in Fig. 4 is -119 cal cm^{-3} for the scandium(III) chelate and -153 cal cm^{-3} for the yttrium(III) chelate. Since C_{ww} is a constant, C'_{ws} for the yttrium(III) chelate is larger than that for the scandium(III) chelate. This suggests that the interaction of yttrium(III) chelate with water is stronger than that of scandium(III) chelate, and this is supported by the structure of the crystalline solid chelates; the scandium(III) chelate is anhydrous and has a coordination number of six [12], and the yttrium(III) chelate has two coordinated water molecules and a coordination number of eight [14]. It is reasonable to consider that an extraction enhancement of yttrium(III) observed in the 1-octanol system results from the replacement of a coordinated water in yttrium(III) chelate with a donating organic solvent such as 1-octanol.

The partition coefficients of the acetylacetonate chelates of scandium(III) and yttrium(III) were compared with those of lanthanoid(III) [4]. Figure 5 shows the plots of $\log P_M$ in the benzene system against the reciprocal of the ionic radius (r) of the central metal [15]. It appears that the partition coefficients linearly increase with an increase in $1/r$, and yttrium(III) chelate is in a position between terbium(III) and thulium(III) chelate. A normal relationship between the formation constant and Z^2/r is known for some rare earth complexes [9]. Here the partition coefficients of the acetylacetonate chelates are plotted against their successive formation

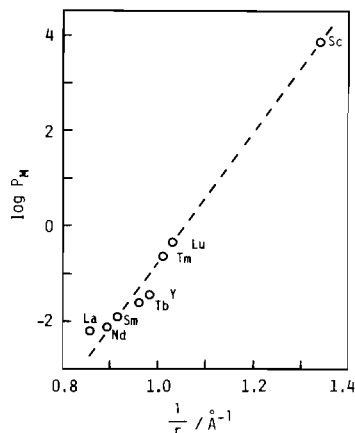


Fig. 5. Correlation between the partition coefficients of tris(acetylacetonato)rare earth(III) chelates and the reciprocal of their ionic radii. The P_M values for lanthanoid(III) were cited from a previous paper [4].

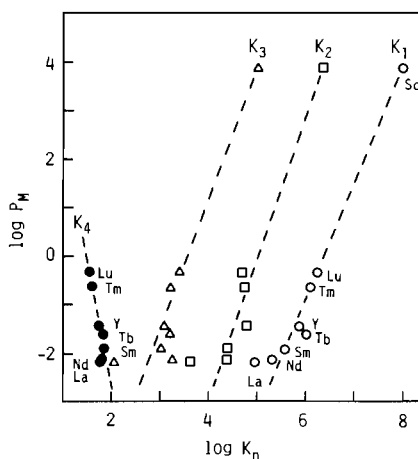


Fig. 6. Correlation between the partition coefficients of tris(acetylacetonato)rare earth(III) chelates and the successive formation constants. The values of P_M , K_2 , and K_3 for lanthanoid(III) is cited from a previous paper [4]. The value of K_1 is cited from the literature [9].

constants K_n , as shown in Fig. 6. Although a small deviation is found, especially for lanthanum(III), a linear correlation between $\log P_M$ and $\log K_n$ is clearly observed. The partition coefficients increase with an increase in the successive formation constant of K_1 , K_2 , and K_3 ; that is, the higher the formation constant of the chelate, the higher the partition coefficient. On the other hand, the partition coefficients decrease with an increase in the K_4 value; that is, the higher the formation constant of the anionic 1:4 chelate, the lower the partition coefficient of the 1:3 chelate. A linear correlation between the partition coefficient and the formation constant may be attributed to the nature of the bond between the central metal and the chelating ligand [16]. In more stable neutral chelates, the positive charge of the

central metal may be effectively neutralized with a greater electron transfer from the ligand, so that the tris chelate with a higher formation constant has little ability to accept the further coordination of an additional donor such as water and its partition coefficient will be high; also this chelate shows little tendency to accept an additional acetylacetonate to form the higher 1:4 complex.

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