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A Regularity of the Liquid–Liquid Partition Coefficients of Tris(acetylacetonato) Rare Earth(III) Chelates

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Abstract

The extraction of La(III), Nd(III), Sm(III), Tb(III) and Lu(III) with acetylacetone in benzene has been studied. The partition coefficients of these tris(acetylacetonato) rare earth(III) chelates do not show the same value but increase as the atomic number of rare earth increases. From comparison of the experimental partition coefficient with the theoretical partition coefficient for the tris-acetylacetonato metal(III) chelate estimated from the regular solution concept and the cavity formation energy, this tendency is ascribed to the gradual decrease of the hydration of the neutral chelate in the aqueous phase.

Introduction

Solvent extraction is one of the powerful separation methods and widely used in basic analytical chemistry and in applied fields of science such as hydrometallurgy of rare metals and reprocessing of nuclear fuel. In the typical chelate extraction process of metal ions, the extraction process can be explained simply by considering the following two key steps, *i.e.* (a) the neutral chelate formation between the metal ion and the acidic chelating agent in an aqueous phase and (b) the partition of the extractable chelate into an organic phase. However, despite the great advance of coordination chemistry on chelate formation in an aqueous solution, we have not enough information on the liquid–liquid partition of the metal chelate. It is a surprising fact that we can not find any description on the liquid–liquid partition of the extractable chelate in the authentic literature on the solvent extraction chemistry. Recently, certain researchers in the environmental science have paid special attention to the use of the liquid–liquid partition coefficient of nonelectrolyte as a simple measure of the migration of such a nonelectrolyte into a living body [1].

We have carried out systematic studies on the solvent effect governing the partition of nonelectrolytes including metal chelates over 20 years and discussed, quantitatively, the regularity of partition coefficients of the homologous series of aromatic compounds and different types of chelates in a series of organic solvents. We have also discussed the role of the aqueous phase by comparing the partition coefficients in the nonaqueous two-phase system of nonpolar solvent and polar solvent [2, 3]. It was also clear that the partition coefficient of the neutral chelate MA_n between metal ion M^{n+}, with different oxidation state, and the acidic chelating agent HA is largely influenced by the nature of the central metal and of the chelating ligand [4]. To understand the role of the central metal ions, it is be necessary to compare the partition coefficient of metal chelates of the central metal ions which have quite similar chemical natures such as oxidation state and electronic configuration. In the present work, the partition coefficient of the tris(acetylacetonate) chelate of several rare earths (III) are determined and the regularity of the partition coefficient is discussed, herein.

Experimental

Materials and Apparatus

Radioisotopes, ^{140}La, ^{147}Nd, ^{160}Tb, and ^{177}Lu, were produced by neutron irradiation of 5–0.5 mg of each oxide (99.99% purity) in the nuclear reactor (JRR-4) of the Japan Atomic Energy Research Institute at a thermal neutron flux of 5.5×10^{13} n cm^{-2} s^{-1} for 6 h. ^{153}Sm was also produced by neutron irradiation of a small portion of the standard solution of samarium nitrate after evaporating to dryness in an irradiated vial. The radioactive solution of each rare earth element 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 before use.

Acetylacetone was washed with diluted ammonia solution and redistilled after drying. The organic solvents used were purified by ordinary methods [5]. Unless otherwise stated, the reagents used were of guaranteed reagent grade.

The γ activity of each radioisotope was measured with an NaI(Tl) well-type scintillation detector

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connected with a single-channel analyzer. The extraction vial was shaken with a mechanical shaker at 330 strokes per minute. The pH value of the equilibrated aqueous phase was measured with a glass electrode.

Procedure

An aqueous solution (6 ml) containing 10^{-7}–10^{-5} M RE(III), labelled with its radioisotope, was placed in a 30 ml centrifuge tube with a ground glass stopper. An organic solution (6 ml) containing 10^{-1} M acetylacetone was added and shaken for 1–3 h at 25 °C and centrifuged. An aliquot was taken from each phase, the γ-activity was measured, and the distribution ratio of RE(III) was calculated as the radioactivity ratio. The pH value of the aqueous phase was adjusted with 5×10^{-3}–10^{-2} M piperazine-N,N′-bis-(2-ethanesulfonic acid) and sodium hydroxide solution, and the equilibrium pH value was measured immediately after shaking. These buffer components were selected carefully to avoid undesirable complex formation with RE(III). Ion strength was adjusted to 0.1 with sodium perchlorate. The shaking time and the concentration of the buffer components were the same as those for Tm(III), reported previously [6].

Results and Discussion

It is practically impossible to measure the partition coefficient of tris(acetylacetonate) chelate of rare earths(III), directly by measuring the liquid–liquid partition of the synthetic tris(acetylacetonato) rare earth(III) mainly because of its dissociative nature in solution. Here, the partition coefficient is determined by analyzing the extraction curve of rare earth (RE) with acetylacetone.

The distribution ratio (D_0) of a tervalent cation, M^{3+}, with a chelating extractant, HA, can be expressed as

$$D_0 = \frac{[\overline{MA_3}]}{[M^{3+}] + \Sigma[MA_n^{3-n}]} = \frac{P_M\beta_3[A^-]^3}{1 + \Sigma\beta_n[A^-]^n} \qquad (1)$$

where the bar denotes the organic phase, β_n the formation constant of MA_n^{3-n} in the aqueous phase, P_M the partition coefficient of MA_3, and A^- the chelating anion in the aqueous phase.

The extraction of La(III), Nd(III), Sm(III), Tb(III) and Lu(III) with Hacac in benzene was carried out and the plots of the logarithmic values of the distribution ratio against the logarithmic values of the concentration of $acac^-$ in the aqueous phase are given in Fig. 1, together with those for Tm(III) as reported previously [6]. The concentration of $acac^-$ was calculated as

$$[A^-] = \frac{C_{HA}}{(P_{HA} + 1)[H^+]/K_{HA} + 1} \qquad (2)$$

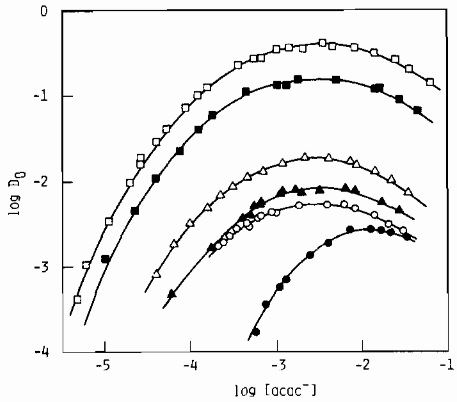

Fig. 1. Distribution ratio of RE(III) as a function of the acetylacetonate ion concentration. Solvent: benzene, ●: La, ○: Nd, ▲: Sm, △: Tb, ■: Tm, □: Lu.

where P_{HA} and K_{HA} denote the participation coefficient and the acid dissociation constant of Hacac, respectively, and C_{HA} the initial concentration. The literature values of P_{HA} and K_{HA} were adopted, *i.e.* $\log P_{HA} = 0.74$ for benzene [7], and $\log K_{HA} = -8.88$ [8]. Both values have been given in the same experimental conditions as this work with an ion strength of 0.1 and at 25 °C.

The plots for each RE(III) give a curve with a maximum. This may indicates the stepwise chelate formation of RE(III) with the increase of $acac^-$ concentration in the aqueous phase, such as $RE(acac)^{2+}$, $RE(acac)_2^+$, $RE(acac)_3$, and $RE(acac)_4^-$. A lowering of the distribution ratio in the higher concentration range of $acac^-$ can be accounted for the formation of $RE(acac)_4^-$. The formation of this higher complex was confirmed by the ion-pair extraction with tetraphenylarsonium cation in Tm(III)–Hacac–chloroform systems [6].

Therefore, the eqn. (1) is rewritten as

$$D_0 = \frac{P_M}{1/k_1k_2k_3[A^-]^3 + 1/k_2k_3[A^-]^2 + 1/k_3[A^-] + 1 + k_4[A^-]} \qquad (3)$$

where k_n (n = 1–4) is the successive formation constant of $RE(acac)_n^{3-n}$ in the aqueous phase. The values of P_M and k_n were computed by the least-squares fitting method, using the computer program SALS (University of Tokyo). These values for each RE(III) are shown in Table I. The reliable values of k_1 for La(III), Nd(III), Sm(III) and Tb(III) and k_2 for Tb(III) are not given in Table I, and this may be ascribed to the presence of only a small fraction of M^{3+} and MA^{2+} under the present experimental concentration range of $acac^-$. The logarithmic values of k_2 and k_3 thus obtained are nearly within 0.3 to those quoted in the literature [9]. It can be reasonably accepted that the values of k_2 and k_3 increase

TABLE I. Equilibrium Constants in RE(III)–Hacac–benzene System.

RE(III)	log P_{MA_3}	log k_1	log k_2	log k_3	log k_4
La	−2.17	–	3.59	2.03	1.76
Nd	−2.12	–	4.39	3.26	1.80
Sm	−1.89[b]	–	4.38	3.02	1.84
Tb	−1.60	–	–	3.22	1.83
Tm[a]	−0.63	5.30	4.74	3.22	1.79
Lu	−0.32	5.27	4.67	3.40	1.56

[a] From ref. 6. [b] −2.45 for carbontetrachloride and −4.57 for heptane.

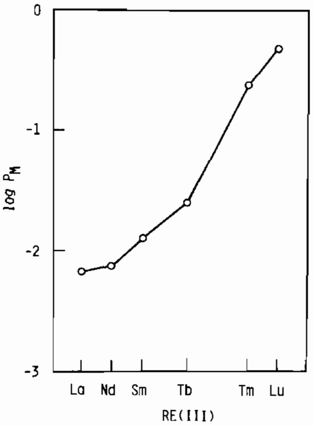

Fig. 2. Plots of the partition coefficient of RE(acac)$_3$ against the atomic number of rare earth elements.

with the increase of the atomic number of RE(III). The values of k_4, which have not been reported, are also given in Table I and are nearly of the same magnitude for these rare earth elements.

The logarithmic values of the partition coefficients of RE(acac)$_3$ are plotted in the order of the atomic number of RE(III) in Fig. 2. These values of P_M increase with the increase of the atomic number of RE(III) and a large difference of 1.85 in the logarithmic scale between the P_M for La(III) and for Lu(III) is observed.

The basic equations expressing the liquid–liquid partition coefficient of a nonelectrolyte c were introduced in 1964 by using the regular solution theory [7] as

$$\log P_c = \frac{V_c}{2.30RT}(\delta_a + \delta_{org} - 2\delta_c)(\delta_a - \delta_{org}) \tag{4}$$

where V and δ denote molar volume and the solubility parameter, respectively, and subscripts 'a' and 'org' the aqueous and organic phase, respectively, when considering the partition of metal chelate MA_n, if the same type of eqn. (4) holds good for a nonelectrolyte chelating agent HA and for a nonelectrolyte metal chelate MA_n, we can arrive at the simple but important relation [10] as

$$\log P_{MA_n} = \frac{V_{MA_n}}{V_{HA}} \log P_{HA} + \text{const.} \tag{5}$$

This is a linear free energy relationship of the partition coefficients of nonelectrolytes HA and MA_n. Eqn. (5) was confirmed experimentally for several types of metal chelates [2, 3]. In the original eqn. (5) the constant term in the righthand side of eqn. (5) is a correction factor for the experimental condition and, ideally, this constant can be neglected [7]. It was also noted that the molar volume ratio of metal chelate and chelating agent V_{MA_n}/V_{HA} is not equal to a simple integer n corresponding to a number of chelating ligands coordinated to metal ions but nearly 0.9 n. There is practically no difference in the molar volume of tris chelate with different central metal ions [3, 4, 10]. From these simple deductions we can expect the partition coefficient of RE(acac)$_3$ to be $0.9 \times 3 \times \log P_{HA}$. But, as acetylacetone is a tautomeric mixture of keto and enol types, it should be compared to the partition coefficient of the enol type of acetylacetone. We already accept the partition coefficient of the enol type of acetylacetone in benzene solvent as 1.5 in log. scale [4, 11, 12]. Hence, the intrinsic partition coefficient of RE(acac)$_3$ would be 4.0 in the log. scale.

We can predict, independently, the intrinsic partition coefficient of a rigid sphere molecule c from the difference between the cavity formation working of the molecule in aqueous solution and that of the same molecule in the organic solution, $\Delta\bar{G}_{cav}$, *i.e.*:

$$\ln P_c = \frac{\Delta\bar{G}_{c,cav}}{RT} \tag{6}$$

The cavity formation energy $\bar{G}_{cav}$ can be evaluated by the scaled particle theory [4] as

$$\bar{G}_{cav} = -RT\ln(1-y) + RT\frac{3y}{1-y}\left(\frac{\sigma_2}{\sigma_1}\right) + RT\left[\frac{3y}{1-y} + \frac{9}{2}\left(\frac{y}{1-y}\right)^2\right]\left(\frac{\sigma_2}{\sigma_1}\right)^2 + \frac{NyP}{\rho}\left(\frac{\sigma_2}{\sigma_1}\right)^3 \tag{7}$$

where σ_1 and σ_2 refer to the molecular radii of solvent and solute, N to Avogadro's number, P to pressure, ρ to number density, and $y = \pi\rho\sigma_1^3/6$. According to this equation, the intrinsic partition coefficient of RE(acac)$_3$ between the aqueous solution and benzene must be 3.8 in the log. scale [4]. This is very close to the intrinsic partition coefficient 4.0 predicted independently from the regular solution concept as discussed above.

Now, this must be compared with the experimental partition coefficient. The highest partition coefficient of RE(acac)$_3$ obtained, experimentally is -0.32 (log. scale) for Lu(acac)$_3$, but is quite small compared to the expected partition coefficient for tris-chelate with acetylacetone at the same aqueous–benzene system. Furthermore, quite a large difference in the experimental partition coefficient for different rare earths(III) cannot be explained simply from the theoretical consideration of the intrinsic partition coefficient. This apparent discrepancy must be due to an additional interaction between the solute chelate and the solvent molecule. Unfortunately, such an interaction cannot be evaluated theoretically, at present. Hence, in the present work, we discuss such a discrepancy by comparing the apparent activity coefficient.

The activity of a nonelectrolyte solute in a nonpolar solvent, a_c, can be expressed as based on the regular solution theory [13]

$$\ln a_{c,o} = \ln X_{c,o} + \frac{V_c}{RT}\phi_o{}^2(\delta_c - \delta_o)^2 \tag{8}$$

where X, V, ϕ and δ are the mole fraction, the molar volume, the volume fraction and the solubility parameter, respectively, and the subscripts, c and o, denote the solute and the organic solvent, respectively. Since the concentration of the solute is very low in the present experiments, ϕ_o is, approximately, a unity. Thus, the activity coefficient of the solute, γ_c, can be expressed as:

$$\ln \gamma_{c,o} = \frac{V_c}{RT}(\delta_c - \delta_o)^2 \tag{9}$$

In order to evaluate the activity coefficient in a nonpolar solvent by eqn. (9), the solubility parameter of the solute must be known. We are attempting to estimate the solubility parameter as follows: the partition coefficient of a solute in mole fraction units, P_c^x, related to the activity coefficient as

$$P_c^x = \frac{X_{c,o}}{X_{c,a}} = \frac{\gamma_{c,a}}{\gamma_{c,o}} \tag{10}$$

where the subscript, a, denotes the aqueous phase. From eqns. (9) and (10), the following equation is derived,

$$\ln P_c^x = -\frac{V_c}{RT}(\delta_c - \delta_o)^2 + \ln \gamma_{c,a} \tag{11}$$

therefore:

$$\frac{RT}{V_c}\ln P_c^x + \delta_o{}^2 = 2\delta_c\delta_o + \left(\frac{RT}{V_c}\ln \gamma_{c,a} - \delta_c{}^2\right) \tag{12}$$

Since the second term of the right hand side of eqn. (12) is independent of the organic solvent, the solubility parameter of the solute, δ_c, can be calculated from the slope in the plots of the left hand side against δ_o for various organic solvents. The partition coefficients of Sm(acac)$_3$ into carbon tetrachloride and heptane were determined from the extraction curve analysis using the same treatment for the benzene system. The plots of log D_0 against log [acac$^-$] are shown in Fig. 3. The concentration of acac$^-$ in the aqueous phase was calculated from eqn. (2), in which the value of P_{HA} was quoted as $10^{0.50}$ for carbon tetrachloride [7] and $10^{-0.05}$ for heptane [11]. The values of P_M of Sm(acac)$_3$ in both solvent systems were calculated from eqn. (3) using successive chelate formation constants, listed in Table I. The solid lines in Fig. 3 represent the extraction curves calculated from eqn. (3) using the determined values of P_M and k_n and a good agreement with the experimental data is observed. The plots of eqn. (12) for benzene, carbon tetrachloride and heptane are shown in Fig. 4 and a good linear relationship is observed. In the calculation of the left hand side of eqn. (12), the molar volume of Sm(acac)$_3$ was presumed to be equal to that of Tm(acac)$_3$, 269 cm^3 mol^{-1} [6]. The solubility para-

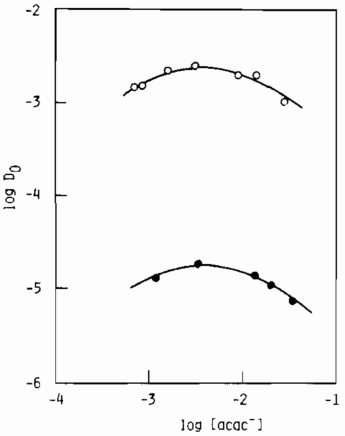

Fig. 3. Distribution ratio of Sm(III) as a function of the acetylacetonate ion concentration. Solvent ○: carbon tetrachloride, ●: heptane.

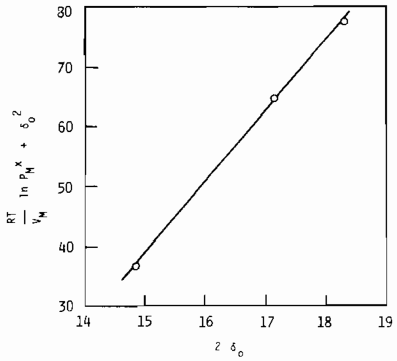

Fig. 4. Plots of eqn. (12) for Sm(acac)$_3$ in different solvent systems. δ_o: 9.16 (benzene), 8.58 (carbon tetrachloride) and 7.43 (heptane).

meter of $Sm(acac)_3$ can be obtained from the slope by the least-squares method as 11.96 $cal^{1/2}cm^{-3/2}$. This value is much closer to that of $Tm(acac)_3$, 12.03 $cal^{1/2}cm^{-3/2}$ [6]. The activity coefficient of $Sm(acac)_3$ in benzene, calculated from eqn. (9) is 3.56 as ln $\gamma_{c,o}$ and close to that of $Tm(acac)_3$, 3.74. This means that there is no noticeable difference between a solution behavior of $Sm(acac)_3$ in the organic phase and that of $Tm(acac)_3$ in the same organic phase. In other words, a quite large difference among the partition coefficients of $RE(acac)_3$ chelates, as shown in Fig. 1 cannot be responsible for a difference in the solution behavior in the organic phase.

The activity coefficient of the chelate in the aqueous phase can be estimated by the simple relationship of eqn. (10). The ln $\gamma_{c,a}$ for $Sm(acac)_3$ is 0.80, but 3.88 for $Tm(acac)_3$. This suggests that Sm-$(acac)_3$ has larger interaction with water than Tm-$(acac)_3$. It is well known that the tris-acetylacetonate chelate of RE(III) easily forms the hydrate. For instance, $La(acac)_3$ dihydrate [14] and $Yb(acac)_3$ monohydrate [15] have been isolated and the coordination numbers of the central metals have been reported to be seven and eight from X-ray diffraction. It has also been reported that the trisacetylacetonate chelate of RE(III), with a higher atomic number, forms the trihydrate and tends to release two water molecules in the vapour pressure experiment [16]. Accordingly, the difference in the partition coefficients of a series of $RE(acac)_3$ may be mainly due to the difference in the interaction between $RE(acac)_3$ and water in the aqueous phase. Therefore, it can be considered that this type of interaction decreases with the increase of the atomic number and with the decrease of the ionic radii of RE(III) in the tris(acetylacetonate) chelate, a very interesting and important regularity of the partition coefficients of tris-chelates. Hence, if the water molecule in the chelate can be replaced by a neutral basic ligand, the extraction efficiency of RE(III) with β-diketon can be highly improved as with the synergic extraction [17, 18].

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