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Complexation of Lanthanoid(III) with Substituted Benzoic or Phenylacetic Acids and Extraction of These Acids

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The stability constants of lathanoid(III) complexes with several benzoic and phenylacetic acids substituted with -OH, -OCH$_3$, or -NH$_2$ groups as well as the dissociation constants of these acids have been determined potentiometrically in 0.1 mol dm^{-3} sodium perchlorate solution at 25 °C. The distribution constants of these acids between the perchlorate media and chloroform and the dimerization constants in chloroform were also determined. The distribution constants of ortho-substituted benzoic acids seem to be larger than those of α-substituted phenylacetic acids with the same substituent. There is a trend that the higher the pK_a, the larger the dimerization constant. The order of pK_a is : *o*-aminobenzoic>*o*-methoxybenzoic>β-hydroxy-β-phenylpropanoic>α-hydroxyphenylacetic(mandelic)>α-methoxyphenylacetic>*o*-hydroxybenzoic acid and the sequence of the stability constants of their complexes for a given lanthanoid is also in a same order except for the mandelate. Mandelic acid forms more stable complexes with the heavier lanthanoid(III) while others are similar to each other regardless of the lanthanoid.

Most α-hydroxy carboxylic acids have been used as eluents in the mutual separation of lanthanoid(III) by ion-exchange method, because these form more stable complexes with the heavier lanthanoid(III). It has also been reported that most carboxylic acids, such as benzoic acid[1] and benzilic acid (α-hydroxydiphenylacetic acid[2]), form adducts with tris(β-diketonato)lanthanoid(III) in organic solvents.

However, it is not always clear what properties of the acids are effective to form stable complexes with lanthanoid(III) in organic and in aqueous solutions. In order to get some information about this point, the effect of the characteristics of acids such as the acid strength, the structure, and the nature of the functional group on the liquid–liquid distribution and the dimerization constants has been examined, using several benzoic and phenylacetic acids substituted with -OH, -OCH$_3$, or -NH$_2$ group at the 2-position of the parent acids. Furthermore, the stability constants of these complexes with lanthanoid(III) have been determined potentiometrically.

Experimental

Reagents. All reagents used were of analytical grade. Mandelic acid (α-hydroxyphenylacetic acid) and tropic acid (β-hydroxy-β-phenylpropanoic acid) were obtained from Nacalai Tesque, Inc., salicylic acid (*o*-hydroxybenzoic acid) and anthranilic acid (*o*-aminobenzoic acid) from Kanto Chemicals, *o*-anisic acid (*o*-methoxybenzoic acid) from Tokyo Kasei Co., and α-methoxyphenylacetic acid from Aldrich Chemical Co. Lanthanoid oxides(III) were obtained from the following companies: Aldrich Chemicals (lanthanum), Mitsuwa Chemicals (neodymium, europium, thulium), Shin-Etsu Chemical Co. (praseodymium, samarium, and lutetium), and American Potash & Chemical Corporation (others). The purity of each oxide was 99.99%. Sodium perchlorate was prepared from sodium carbonate and perchloric acid; it was recrystallized twice from water. Chloroform was washed three times with deionized water. The other reagents were employed without further purification.

Procedures. All the procedures were carried out in a thermostated room at 25 °C. The total anion concentration was adjusted to 0.1 M (1 M=1 mol dm^{-3}) with sodium perchlorate. The solution containing 0.010 M HClO$_4$+0.09 M NaClO$_4$ solution was employed as the standard of $-\log[H^+]=2.00$ (hereafter $-\log[H^+]$ is abbreviated as pC$_H$).

i) Dissociation, Distribution, and Dimerization Constants of the Carboxylic Acids.

Dissociation Constants of Carboxylic Acids. A certain volume (about 50 cm^3) of a buffered carboxylic acid solution ($[A^-]/[HA]=1$), in other words, the acid solution in which a half of the acid was neutralized with sodium hydroxide, was titrated with perchloric acid potentiometrically. The total acid concentration was about 0.02 M. The other dissociation constant of anthranilic acid owing to the amino group associated with proton, K_a' ($=[H^+][HA]/[H_2A^+]$), was similarly determined by titrating the acid solution, in which perchloric acid equivalent to a half concentration of the total anthranilic acid had been added, with sodium hydroxide solution. The titrations were repeated several times. In all cases, the repetitive runs agreed satisfactorily.

Distribution and Dimerization Constants of the Acids. A portion of chloroform solution containing one of the acids at various concentrations and an equal volume of 0.1 M sodium perchlorate solution adjusted to a certain pC$_H$ were placed in a stoppered glass tube and the two phases were agitated vigorously. After then, the mixtures were centrifuged. The pC$_H$ in the aqueous solution was measured. The acid concentrations in the aqueous phases were determined by measuring the absorbance at a certain wavelength, near the wavelength giving the maximum absorbance, e.g., for salicylic acid, at 301.7 nm where the molar absorptivity was 3.53×10^3, and for mandelic acid at 260 nm (the absorptivity was 1.64×10^2). The concentration in the organic phases was also determined by measuring the absorbance directly except for anthranilic acid. The molar absorptivity was 4.10×10^3 at 309 nm for salicylic acid, and 1.85×10^2 for mandelic acid at 260 nm. The concentration of anthranilic acid in chloroform was determined from the absorbance after back-extraction into sodium hydroxide solution. The molar absorptivity of anthranilic acid at the wavelength was constant at $pC_H>7$. However, at lower pC_H, the absorptivity decreased.

The distribution ratio is defined as,

$$D = [HA]_{org,total}/[HA]_{aq,total}$$

hereafter, the organic phase is denoted by the subscript "o" and the aqueous phase has no subscript. The distribution ratio of the monocarboxylic acid can generally be represented as follows:

$$D = \frac{[HA]_o + 2[(HA)_2]_o}{[HA] + [A^-]} = \frac{K_d(1 + 2K_dK_{dim}[HA])}{1 + K_a/[H^+]} \quad (1)$$

where K_d is the distribution constant of the acid ($K_d=[HA]_o/[HA]$) and K_{dim} is the dimerization constant ($K_{dim}=[(HA)_2]_o/[HA]_o^2$).

The distribution ratio was also measured at various pC_H for each acid at 1.0×10^{-3} M.

ii) Stability Constants of the Complexes. The metal(III) solutions were prepared by dissolving the respective weighed oxide in perchloric acid. The lanthanoid(III) concentration was determined by titration with EDTA using Xylenol Orange as the indicator at about $pC_H=5$. The pC_H in the metal(III) solution was adjusted, just prior to use to a similar pC_H in the buffered ligand acid solution in order to avoid the change in the pC_H due to the acid-base neutralization. The stability constants of the lanthanoid(III) complexes were determined by titrating the metal(III) solutions with the half-neutralized carboxylate solution potentiometrically. The potentiometric titration data were analyzed using the following equation based on the Bjerrum formation function.

$$\frac{\bar{n}}{1-\bar{n}} \cdot \frac{1}{[A^-]} = \beta_1 + \beta_2 \frac{2-\bar{n}}{1-\bar{n}} [A^-] \quad (2)$$

where $\bar{n}$ is the average number of ligands combined with the metal ion. More detailed data treatment is reported elsewhere.[8]

Results and Discussion

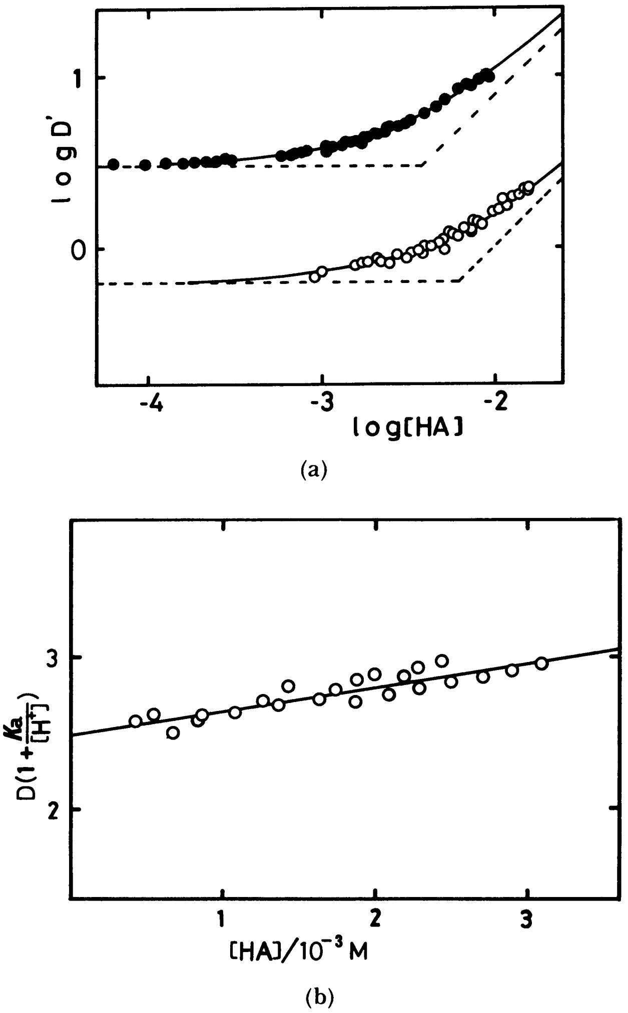
i) Dissociation, Distribution, and Dimerization Constants of the Carboxylic Acids. The pK_a values obtained by potentiometric titration are listed in Table 1. Since the pK_a of the parent acids, i.e., benzoic and phenylacetic acids, is almost 4,[6,7b] the introduction of these functional groups decreases the values of pK_a except for $-NH_2$. The values of the dissociation constant obtained in the present work agree with the several results reported earlier.[7] The pK_a of salicylic acid reported in the literature scatters. However, a value which agrees with the present result, (2.70±0.02 in 0.10 M ionic medium), has also been reported.[8]

Figure 1-a shows the log–log plots of the distribution ratio of salicylic and anthranilic acids against the undissociated acid concentration in the aqueous phase. Since the distribution ratio depends on the pC_H as given in Eq. 1, the pC_H at equilibrium was measured and $\log D(1+K_a/[H^+])$ for salicylic acid and $\log D(1+K_a/[H^+]+[H^+]/K_a')$ for anthranilic acid instead of $\log D$ are plotted against log[HA]. The undissociated acid concentration was calculated from the total acid concentration in the aqueous phases (A_T) and the K_a, according to $[HA]=A_T/(1+K_a/[H^+])$ while that of anthranilic acid was calculated according to $[HA]=A_T/(1+K_a/[H^+]+[H^+]/K_a')$. The data were analyzed by a curve-fitting method using a normalized curve, $Y=\log(1+v)$ where $v=2K_d\times K_{dim}[HA]$ (see Eq. 1). Consequently, K_d and K_{dim} were obtained. Since the distribution ratio could not be determined over a wide range of [HA] for the other acids (due to the restriction of solubilities), the relation in Eq. 1 was plotted in antilog units (an example is shown in Fig. 1-b) and from the intercept and the slope of the straight lines obtained, the constants were determined. All the constants obtained are listed in Table 1. The solid curves in Fig. 1 were calculated using the constants obtained. The curves fit well to the data.

Table 1. Equilibrium Constants of Acids
Aqueous Solution : 0.1 M $NaClO_4$
Organic Solvent : $CHCl_3$

Acid	pK_a	$\log K_d$	$\log K_{dim}$
Salicylic (*o*-Hydroxybenzoic)	2.72	0.48	1.64
Anisic (*o*-Methoxybenzoic)	3.92	1.58	—
Anthranilic (*o*-Aminobenzoic)	4.68 (2.15)[a]	−0.20	2.15
Mandelic (α-Hydroxyphenylacetic)	3.18	−1.47[4]	1.50[4]
α-Methoxyphenylacetic	2.97	0.40	1.10
Tropic (β-Hydroxy-β-phenylpropanoic)	3.90	−1.09	1.54
Benzoic	4.01[6]	0.44[5]	2.22[5]

a) In the parentheses $K_a'=[HA][H^+]/[H_2A^+]$.



(a)

(b)

Fig. 1. Typical examples of extraction curves as a function of undissociated acid concentration in aqueous phases. a) Log-log plot of distribution ratio of salicylic and anthranilic acids as a function of [HA]. The $-\log[H^+]$ is around 2.0 for salicylic acid (●) and 3.4 for anthranilic acid (○). $\log D' = \log D(1+K_a/[H^+])$ for salicylic acid and $\log D' = \log D(1+K_a/[H^+]+[H^+]/K_a')$. The dotted lines are $Y = \log K_d$ and $Y = \log[HA] + \log 2K_d^2K_{dim}$. b) Distribution ratio of α-methoxyphenylacetic acid against [HA]. The solid line is $Y = 2.49 + 1.57 \times 10^2[HA]$. The correlation coefficient is 0.89_4. The $-\log[H^+]$ is around 2.0.

In order to ascertain the validity of Eq. 1 and of applying pK_a, which was determined in 0.1 M sodium perchlorate media without saturation with chloroform, to the analysis of the solvent extraction data, the distribution ratio was measured at various pC_H at a constant acid concentration. Figure 2 shows the plots of the distribution ratio of salicylic, anthranilic, and mandelic acids against pC_H using a total acid concentration of 10^{-3} M. The solid curves are calculated from Eq. 1 using all the constants in Table 1. The curves fit well to the data. The data obtained by similar experiments with other acids fitted well to the values calculated from the constants obtained. The fact that all the constants, including pK_a, explain the data well would suggest that the constants obtained in an aqueous solution without saturation with organic solvents can be applied to solvent extraction data.

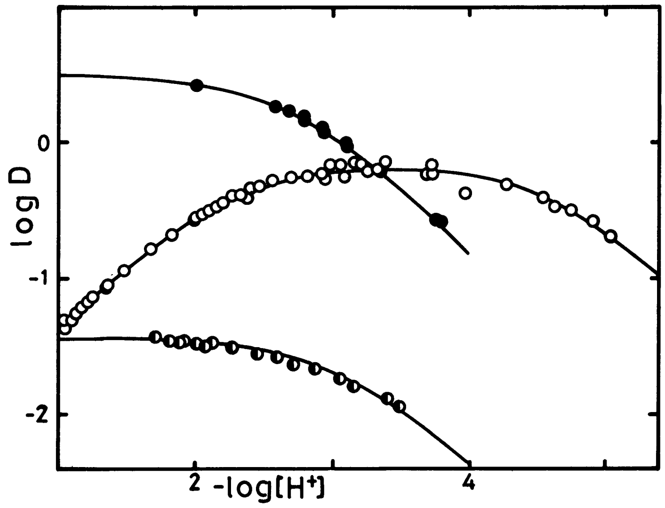


Fig. 2. Distribution ratio of salicylic, anthranilic, or mandelic acid as a function of $-\log[H^+]$. Total acid concentration: 1.0×10^{-3} M. Aqueous phase: 0.1 M $NaClO_4$, organic phase: $CHCl_3$. Salicylic (●), anthranilic (○), and mandelic (◐) acids.

As seen from Table 1, it is not easy to find definite correlation among pK_a, K_d, and/or K_{dim}. The distribution constants of the substituted benzoic acids seem to be larger than those of the phenylacetic acids substituted with the same functional group. There is a trend that the higher the pK_a, the larger K_{dim}, at least in the family of phenylacetic acid. The trend would be explained as: the acid anion capable of attracting hydrogen ion strongly, i.e., the oxygen atom in carboxyl group to be the stronger Lewis base, may also attract a hydrogen atom in other acid molecules to form a hydrogen bond. This result suggests that a carboxylic acid having higher pK_a may form more stable adducts with lanthanoid(III) chelates such as tris(β-diketonato)lanthanoid(III) in organic phases. The high pK_a and small K_{dim} of *o*-anisic acid may be caused by the methoxyl group at the ortho position. This could form an inner complex with the hydrogen atom in the carboxyl group. Consequently, the dissociation is depressed and the distribution constant is large, due to less hydration. Furthermore it would not easily associate with other *o*-anisic acid, i.e., low K_{dim}. We can not explain the low pK_a, and high distribution and dimerization constants of salicylic acid, most presumably, owing to inner complexation in salicylate ion.

ii) Complexation of Lanthanoid(III) with These Acids. Table 2 gives typical examples of the potentiometric titration data. Using these data, $\bar{n}/((1-\bar{n})[A^-])$ and $(2-\bar{n})[A^-]/(1-\bar{n})$ were calculated (see Eq. 2),

Table 2. Potentiometric Titration Data in 0.10 M ($NaClO_4$) at 25 °C

(1) Terbium(III) anthranilate

Volume of titrant/cm^3	$-\log[\mathrm{H}^+]$	$[\mathrm{A}^-]^{\mathrm{a})}/10^{-4}$ M	$\bar{n}$
3.0	4.25_6	2.15	0.04_1
4.0	4.24_8	2.80	0.05_3
5.0	4.24_3	3.42	0.06_6
6.0	4.24_3	4.06	0.07_8
7.0	4.24_3	4.68	0.09_0
8.0	4.24_4	5.29	0.10_2
9.0	4.24_8	5.92	0.11_3
10.0	4.24_9	6.51	0.12_5
11.0	4.25_3	7.11	0.13_6
12.0	4.25_6	7.70	0.14_7
13.0	4.26_0	8.29	0.15_8

in the cup; initial volume=50.0 cm^3
initial $-\log[\mathrm{H}^+]=4.80_7$
initial terbium(III) concentration=1.02×10^{-2} M
in the buret; titrant concentration=2.08×10^{-2} M

(2) Dysprosium(III) mandelate

Volume of titrant/cm^3	$-\log[\mathrm{H}^+]$	$[\mathrm{A}^-]^{\mathrm{a})}/10^{-4}$ M	$\bar{n}$
6.0	2.75_5	3.51	0.32_1
7.0	2.73_8	4.21	0.36_2
8.0	2.72_3	4.85	0.40_3
9.0	2.71_3	5.54	0.44_1
10.0	2.70_4	6.21	0.47_9
11.0	2.69_7	6.88	0.51_5
12.0	2.69_4	7.60	0.55_0
13.0	2.68_9	8.23	0.58_6
14.0	2.68_9	8.99	0.61_7
15.0	2.68_7	9.67	0.65_0

in the cup; initial volume=50.0 cm^3
initial $-\log[\mathrm{H}^+]=3.19_4$
initial dysprosium(III) concentration=1.03×10^{-2} M
in the buret; titrant concentration=3.96×10^{-2} M

a) Free carboxylate ion concentration at equilibrium.

and the former was plotted against the latter. Straight lines having positive slopes were obtained. The first and second stability constants were determined from the intercept and the slope, respectively. The constants so obtained are listed in Table 3 together with the error limits based on the agreement in repetitive titrations. In these experiments, owing primarily to two reasons, high $\bar{n}$ could not be obtained, that is, i) lanthanoid(III) does not form stable complexes with these ligands except for mandelate ions, and ii) since the solubility of the acids employed in water is not high, the free carboxylate anion concentration at equilibrium was not over 2×10^{-3} M. Consequently, the second stability constants have rather big errors.

It would appear from the values in Table 3 that the order of the stability constants for a given lanthanoid(III) is in the following sequence: mandelates≫anthranilates>o-anisates≃tropates≃α-methoxyphenylacetates≃benzoates>salicylates. This sequence may be due to the differene of pK_a of the ligand acids. Actually, it has been reported⁶⁾ that the correlation between log β_1 and pK_a is linear, when the interaction between lanthanoid ion and a ligand is ionic and there is no variation in the steric effects. Figure 3 shows the correlation between the first stability constants of europium(III) complexes (log β_1) and pK_a of the ligand acid together with that reported for several monocarboxylates in the literature. The constants are classified into two different groups. The α-hydroxy carboxylic acids which may form five-membered chelates belong to the upper group, and other carboxylic acids belong to the lower group. Although α-methoxyphenylacetic acid may form a five-membered ring, it does not belong to the upper group. Similarly, methoxyacetic acid¹⁰⁾ also does not belong to the upper group. In the lower group, the order of the stability constants in magnitude seems to be correlated with the difference of pK_a. Furthermore, as seen in Table 1, only mandelic acid forms more stable complexes with the heavier lanthanoid(III), and the stability constants (log β_1) of the series of lanthanoid(III) complexes with other carboxylic acids employed in the present work are similar to each other.

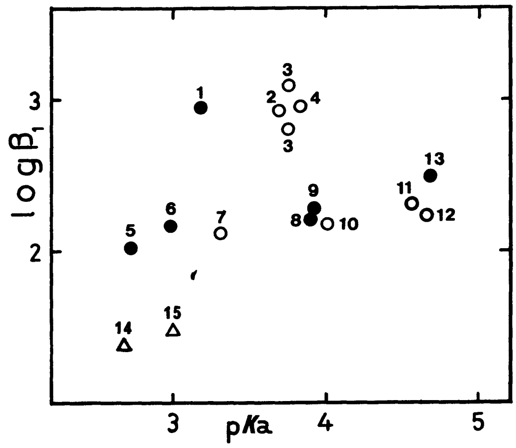


Fig. 3. Correlation between the first stability constants (log β_1) of Eu$^{\mathrm{III}}$ complexes and the dissociation constants of the ligand acids (pK_a). 1. Mandelate, 2. hydroxyacetate, 3. α-hydroxymethylpropanoate, 4. α-hydroxypropanoate, 5. salicylate, 6. α-methoxyphenylacetate, 7. methoxyacetate, 8. β-hydroxy-β-phenylpropanoate, 9. o-methoxybenzoate, 10. benzoate, 11. acetate, 12. propanoate, 13. anthranilate, 14. chloroacetate, 15. iodoacetate, solid circles: present work, open circles: taken from Refs. 6 and 7, triangles: taken from Ref. 9.

In a word, the presence of the OH group at the α-position of carboxylates seems to be very effective to form a more stable complex with the heavier lanthanoid(III). However, β-position of carboxylates, o-position of benzoic acid or other functional group such as methoxyl group are not effective. Further accumulation of data would be necessary in order to know the reason why α-hydroxy carboxylic acids form more stable complexes with the heavier lanthanoid.

Table 3. Stability Constants of Lanthanoid(III) Complexes with Substituted Benzoic and Phenylacetic Acids in 0.1 M $NaClO_4$ at 25 °C

a) -OH substitution

	Mandelate		Salicylate	
	$\log(\beta_1 \pm \delta)$[a]	$\log(\beta_2 \pm \delta)$	$\log(\beta_1 \pm \delta)$	$\log(\beta_2 \pm \delta)$
La	2.55±0.06	4.14±0.08	1.80±0.06	3.55±0.23
Pr	2.76±0.01	4.65±0.08	1.88±0.02	3.70±0.33
Nd	2.83±0.03	4.77±0.12	1.90±0.04	3.56±0.09
Sm	2.90±0.09	4.75±0.08	2.06±0.03	3.82±0.21
Eu	2.95±0.01	5.07±0.13	2.02±0.05	3.84±0.03
Gd	2.88±0.03	5.01±0.15	1.89±0.06	3.78±0.03
Tb	3.01±0.03	5.25±0.05	1.95±0.02	3.86±0.02
Dy	3.03±0.04	5.29±0.08	1.71±0.03	3.76±0.04
Ho	3.05±0.06	5.35±0.09	1.83±0.08	3.79±0.23
Er	3.15±0.07	5.41±0.05	1.78±0.05	3.59±0.17
Tm	3.20±0.07	5.56±0.06	1.75±0.07	3.67±0.08
Yb	3.29±0.01	5.76±0.02	1.78±0.07	3.45±0.06
Lu	3.25±0.03	5.83±0.04	1.65±0.04	3.75±0.05

b) $-OCH_3$ substitution

	α-Methoxyphenylacetate		*o*-Anisate	
	$\log(\beta_1 \pm \delta)$	$\log(\beta_2 \pm \delta)$	$\log(\beta_1 \pm \delta)$	$\log(\beta_2 \pm \delta)$
La	2.09±0.00	3.84±0.12	2.07±0.00	4.05±0.05
Pr	2.16±0.06	3.57±0.23	2.20±0.01	4.17±0.04
Nd	2.16±0.02	3.83±0.06	2.26±0.01	4.20±0.08
Sm	2.24±0.02	3.64±0.10	2.31±0.03	4.22±0.14
Eu	2.17±0.02	4.12±0.22	2.28±0.02	4.26±0.02
Gd	2.14±0.01	3.59±0.17	2.19±0.01	3.99±0.17
Tb	2.19±0.04	3.97±0.20	2.15±0.01	4.12±0.06
Dy	2.19±0.03	3.82±0.11	2.11±0.02	4.08±0.10
Ho	2.19±0.11	3.85±0.26	2.07±0.02	4.06±0.05
Er	2.19±0.02	3.61±0.07	2.06±0.01	3.95±0.03
Tm	2.14±0.03	3.86±0.15	2.05±0.03	4.11±0.08
Yb	2.23±0.05	4.10±0.12	2.06±0.07	3.90±0.17
Lu	2.31±0.05	3.97±0.01	2.10±0.03	4.09±0.14

c) Miscellaneous

	Tropate		Anthranilate	
	$\log(\beta_1 \pm \delta)$	$\log(\beta_2 \pm \delta)$	$\log(\beta_1 \pm \delta)$	$\log(\beta_2 \pm \delta)$
La	2.02±0.07	3.90±0.08	1.96±0.04	4.08±0.08
Pr	2.14±0.01	4.00±0.09	2.33±0.03	4.39±0.04
Nd	2.23±0.05	4.11±0.04	2.44±0.02	4.26±0.17
Sm	2.24±0.06	4.11±0.18	2.44±0.02	4.78±0.05
Eu	2.21±0.01	4.02±0.02	2.49±0.02	4.78±0.05
Gd	2.17±0.02	4.12±0.08	2.36±0.03	4.51±0.17
Tb	2.07±0.02	4.00±0.07	2.28±0.01	4.40±0.10
Dy	2.10±0.01	3.92±0.03	2.27±0.04	4.39±0.10
Ho	2.05±0.02	4.02±0.09	2.17±0.04	4.22±0.12
Er	1.99±0.03	3.93±0.02	2.16±0.04	4.21±0.12
Tm	2.02±0.10	3.78±0.2	2.22±0.01	4.39±0.06
Yb	2.05±0.02	3.98±0.19	2.24±0.00	4.40±0.06
Lu	2.09±0.05	3.97±0.20	2.22±0.03	4.53±0.11

a) δ denotes error limits based on the agreement in repetitive titrations.

The larger stability constants and the monotonical increase of $\log \beta_1$ against the atomic number could be caused by the match of the bond angle of the hydroxyl group and the carboxyl group to the smaller sized lanthanoid(III). In α-methoxy carboxylates, the one carbon and the three hydrogen atoms in the methoxyl group could interfere with taking up an appropriate bond angle to accept lanthanoid(III).

As seen from Fig. 3, the stability constant of the salicylate seems to be a little larger than estimated from the correlation between pK_a and $\log \beta_1$ of monocarboxylates. This may be due to the formation of stable chelates between the salicylic acid and lanthanoid(III),[11] or due to a proper character of salicylate ion.

The above results may suggest that: 1) there is a trend that the acid of higher pK_a has a larger dimerization constant. When the ligand acids are not α-hydroxy carboxylic acids, log β_1 increases in proportion to pK_a. Accordingly, pK_a will be one of the important parameters for the complexation in the organic phases as well as in the aqueous solutions. 2) The behavior of salicylic acid in aqueous and/or in organic solvents including complexation with lanthanoid(III) is different from that of other carboxylic acids. 3) Only carboxylic acids having a hydroxyl group at the α-position are effective to form the more stable complexes with the heavier lanthanoid(III). Other functional groups, and hydroxyl group at the β-position or the *o*-position are not effective.

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References

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

2) Y. Hasegawa, H. Tanaka, A. Kobashi, and T. Tominaga, *Solv. Extr. and Ion Exchange,* **6**, 293 (1988).

3) K. Suzuki, T. Hattori, and K. Yamasaki, *J. Inorg. Nucl. Chem.,* **30**, 161 (1968).

4) Y. Hasegawa, et al. unpublished data.

5) Y. Hasegawa, T. Unno, and G. R. Choppin, *J. Inorg. Nucl. Chem.,* **43**, 2154 (1981).

6) G. R. Choppin, P. A. Bertrand, Y. Hasegawa, and E. N. Rizkalla, *Inorg. Chem.,* **21**, 3722 (1982).

7) a) "Stability Constants of Metal-Ion Complexes," spec. pub. No. 17, compiled by L. G. Sillen and A. E. Martell, The Chemical Society (London) (1964), b) *ibid.,* Supplement No. 1, c) *ibid.,* Part B No. 22, compiled by D. D. Perrin, Pergamon Press, Oxford (1979).

8) G. E. Mont and A. E. Martell, *J. Am. Chem. Soc.* **88**, 1387 (1966).

9) A. E. Martell and R. M. Smith, "Critical Stability Constants," Plenum, New York (1977), Vol. 3.

10) J. E. Powell, R. S. Kolat, and G. S. Paul, *Inorg. Chem.,* **3**, 518 (1964).

11) G. R. Choppin, Q. Liu, and C. Niu, *Lanthanide and Actinide Res.,* **1**, 285 (1986).