

Stability constants of rare earth complexes: citraconate, mesaconate and itaconate complex species

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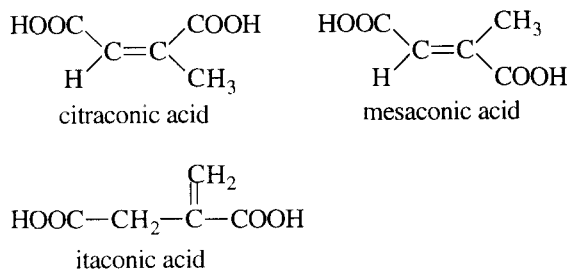
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Abstract

The stability constants of the rare earth complexes with citraconate, mesaconate and itaconate ligands were determined by the potentiometric titration method at 25.0 °C and at an ionic strength of 0.10 with potassium nitrate as supporting electrolyte. The measurements were carried out in solutions containing equimolar amounts of metal and ligand to obtain the stability constants of ML, ML₂ and possible MHL complex species, where M and L denote the metal and the ligand, respectively. The stability constants of the rare earth complexes were in increasing order of mesaconates, itaconates and citraconates. Scandium seemed to form hydroxo complexes under the experimental conditions.

1. Introduction

Citraconic, mesaconic and itaconic acids are dicarboxylic and isomeric, having a carbon–carbon double bond; citraconic and mesaconic acids are *cis* and *trans* isomers, respectively.



The structural configurations of the ligand acids have a considerable effect on the stability of the resulting complex. A few papers on the stability constants of some rare earth complexes with citraconate and itaconate ligands have been reported [1–7], however, mesaconate complexes have not been studied so far. The aim of the present work was to obtain thorough data on the rare earth complexes with the three ligands, and to investigate the effect of the ligand structure on the stability constants.

2. Experimental details

The rare earth stock solutions, except cerium nitrate, were prepared by dissolving the respective oxides of 99.9% or higher purity (Shin-etsu Chem. Ind. Co., Ltd.) in nitric acid. Cerium nitrate solution was prepared by dissolving cerium(III) nitrate. The rare earth nitrate solutions thus prepared were adjusted to the equivalence pH values to have a concentration of 0.050 mol dm⁻³.

All the other chemicals were of reagent grade. The potentiometric titrations and measurements were performed in a thermostatted bath at 25.0 ± 0.1 °C. The pH measurements were carried out with a Denki Kagaku Keiki (DKK) model PHL-40 precision pH meter.

The sample solutions were adjusted to a constant ionic strength (*I*) of 0.10 with potassium nitrate as supporting electrolyte, and were titrated with a carbonate-free standard sodium hydroxide solution. The colloidal precipitates appeared in the titrated solutions of relatively high pH values.

The computation program BEST [8] was used for calculating the stability constants of the species ML, ML₂ and MHL, as well as the acid dissociation constants. Standard deviations of pH calculation, σ_{fit} ($1/N \sum (\text{pH}_{\text{obs}} - \text{pH}_{\text{calc}})^2$), were less than 0.010 throughout the experiments.

3. Results and discussion

The acid dissociation constants were determined by potentiometric titration as shown in Table 1, together

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TABLE 1. Dissociation constants of citraconic, mesaconic, and itaconic acids and related compounds at 25.0 ± 0.1 °C and at $I=0.10$

Acid	pK_{a1}	pK_{a2}
Citraconic	2.50 ± 0.01	5.80 ± 0.01
Mesaconic	3.08 ± 0.01	4.54 ± 0.01
Itaconic	3.74 ± 0.01	5.22 ± 0.01
Fumalic [1]	2.85	4.09
Maleic [2]	1.77	5.85

TABLE 2. Logarithms of stability constants of rare earth complexes with citraconate ligand at 25.0 ± 0.1 °C and at $I=0.10$

Metal ion	ML	ML ₂	MHL
Sc	5.64 ± 0.01	3.96 ± 0.34	1.42 ± 0.27
Y	3.82 ± 0.04	1.91 ± 0.11	3.31 ± 0.20
La	3.71 ± 0.02	2.18 ± 0.07	3.65 ± 0.07
Ce	3.81 ± 0.01	2.21 ± 0.01	3.60 ± 0.01
Pr	3.87 ± 0.02	2.15 ± 0.11	3.47 ± 0.05
Nd	3.88 ± 0.02	2.24 ± 0.09	3.32 ± 0.09
Sm	3.96 ± 0.03	2.05 ± 0.29	3.25 ± 0.03
Eu	3.99 ± 0.04	2.26 ± 0.06	3.21 ± 0.17
Gd	4.00 ± 0.01	2.34 ± 0.15	3.37 ± 0.06
Tb	3.98 ± 0.01	2.27 ± 0.09	3.39 ± 0.07
Dy	3.93 ± 0.02	2.05 ± 0.11	3.30 ± 0.08
Ho	3.91 ± 0.01	2.11 ± 0.08	3.41 ± 0.04
Er	3.89 ± 0.01	2.20 ± 0.12	3.35 ± 0.03
Tm	3.91 ± 0.01	2.44 ± 0.01	3.32 ± 0.09
Yb	3.94 ± 0.03	2.26 ± 0.14	3.44 ± 0.07
Lu	3.96 ± 0.03	2.36 ± 0.11	3.52 ± 0.06

with the reference values for fumalic and maleic acids [9,10]. The first dissociation constants increased in the order of citraconic, mesaconic and itaconic, whereas the second constants were in the order of mesaconic, itaconic and citraconic acids. The lower pK_{a1} and higher pK_{a2} values of citraconic acid may be due to the stabilized cyclic structure through the intramolecular hydrogen bonding of its monovalent anion. The lower dissociation of itaconic acid can be explained by the location of the double bond, which is not in between two carboxylic acid groups as in the cases of citraconic and mesaconic acids.

The stability constants obtained from the titrations at 1:1 metal/ligand ratio are given in Tables 2–4. All three ligands showed similar increasing stability trends as far as the species ML is concerned, with an intermediate decrease at the mid-lanthanides, where the decrease in coordination number has often been pointed out. The stability constants of the yttrium complexes were slightly lower than those of holmium complexes, as expected from the ionic radii.

Since very small amounts of the species ML₂ with mesaconate and itaconate ligands could be formed, the

TABLE 3. Logarithms of stability constants of rare earth complexes with mesaconate ligand at 25.0 ± 0.1 °C and at $I=0.10$

Metal ion	ML	MHL
Sc	4.14 ± 0.02	2.68 ± 0.02
Y	2.49 ± 0.02	3.59 ± 0.01
La	2.49 ± 0.01	3.67 ± 0.02
Ce	2.58 ± 0.02	3.53 ± 0.09
Pr	2.64 ± 0.03	3.54 ± 0.01
Nd	2.71 ± 0.02	3.49 ± 0.01
Sm	2.79 ± 0.01	3.49 ± 0.02
Eu	2.71 ± 0.01	3.53 ± 0.02
Gd	2.67 ± 0.01	3.44 ± 0.02
Tb	2.59 ± 0.01	3.46 ± 0.07
Dy	2.53 ± 0.02	3.48 ± 0.07
Ho	2.54 ± 0.02	3.57 ± 0.04
Er	2.50 ± 0.03	3.41 ± 0.07
Tm	2.54 ± 0.02	3.41 ± 0.07
Yb	2.59 ± 0.01	3.54 ± 0.10
Lu	2.63 ± 0.02	3.58 ± 0.10

TABLE 4. Logarithms of stability constants of rare earth complexes with itaconate ligand at 25.0 ± 0.1 °C and at $I=0.10$

Metal ion	ML	ML ₂	MHL
Sc	5.35 ± 0.01	3.60 ± 0.11	2.77 ± 0.03
Y	3.26 ± 0.01	–	3.47 ± 0.05
La	3.12 ± 0.02	–	3.69 ± 0.03
Ce	3.20 ± 0.01	–	3.48 ± 0.07
Pr	3.33 ± 0.01	–	3.55 ± 0.01
Nd	3.43 ± 0.01	–	3.61 ± 0.05
Sm	3.51 ± 0.01	1.91 ± 0.14	3.59 ± 0.02
Eu	3.52 ± 0.01	1.61 ± 0.46	3.60 ± 0.02
Gd	3.50 ± 0.01	1.78 ± 0.16	3.62 ± 0.07
Tb	3.46 ± 0.01	–	3.62 ± 0.02
Dy	3.41 ± 0.01	–	3.56 ± 0.01
Ho	3.36 ± 0.01	1.92 ± 0.16	3.52 ± 0.02
Er	3.35 ± 0.01	1.90 ± 0.03	3.56 ± 0.01
Tm	3.32 ± 0.02	1.61 ± 0.21	3.49 ± 0.11
Yb	3.33 ± 0.02	1.61 ± 0.39	3.46 ± 0.05
Lu	3.35 ± 0.01	1.95 ± 0.10	3.54 ± 0.03

stability constants of ML₂ could not be obtained for the mesaconates. The distribution of the gadolinium itaconate species in solution are shown in Fig. 1. Similar distribution curves were obtained on the other complexes, except scandium. Although no direct evidence of the species MHL and M(OH)₂ was found, both the acid dissociation diagrams and the computation results supported the formation of the protonated or hydroxo complexes with better accuracy than those without considering these species. Small amounts of the species MHL may possibly be formed in systems with a considerable excess of the species HL[–]. The distribution of divalent mesaconate should refer to the species ML and the amount of free metal ion is greater than in

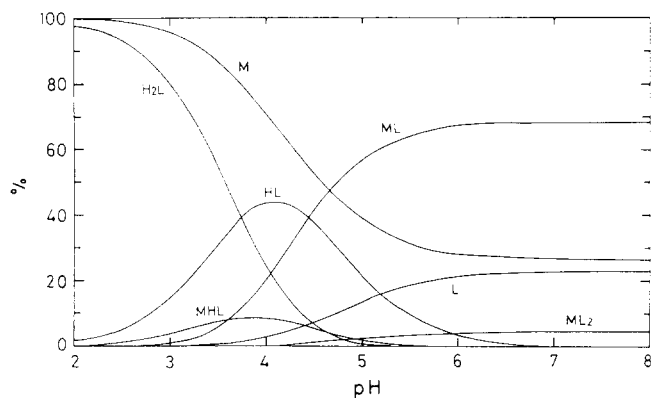


Fig. 1. Distribution of the species in a 1:1 molar ratio of itaconate to Gd^{3+} at 25.0 °C and at $I=0.1$ (KNO_3).

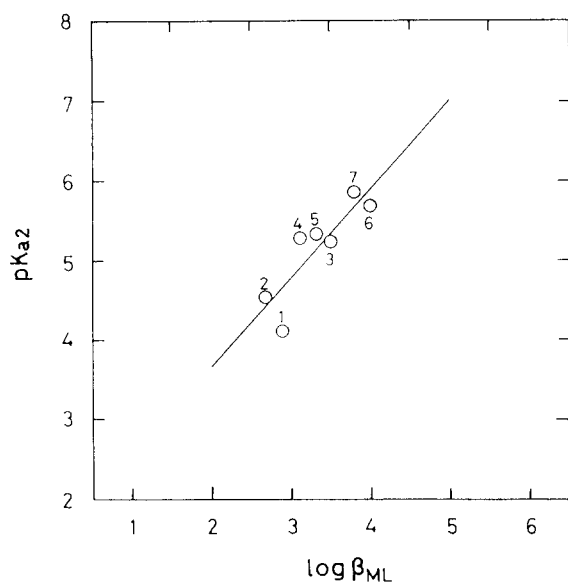


Fig. 2. Correlation between $\log \beta_{ML}$ and pK_{a2} . 1, Fumalate [9,11]; 2, mesaconate; 3, itaconate; 4, succinate [12]; 5, methylsuccinate [10]; 6, citraconate; 7, maleate [10].

the others, thus mesaconate may form ML complexes, but they would not be as stable as those of the other two ligands. Two carboxylate groups can apparently form bonds with a metal ion. Mesoconic acid has two carboxyl groups at the *trans* position, thus a metal ion can be bound to a dissociated carboxylate group; otherwise it could be linked to the ligand indirectly.

The stability constants obtained in the present work were in the increasing order of mesaconates, itaconates and citraconates, and the trends were considered to be related to the basicity of the ligand acids. Figure 2 shows the relation between the basicities of the ligand acids and the stability constants of gadolinium complexes of some dicarboxylates [9–12]. An approximately linear relationship was observed among the values of pK_{a2} and $\log \beta_{ML}$.

The relations between the constants of the scandium, yttrium and lanthanide complexes and the ionic radius,

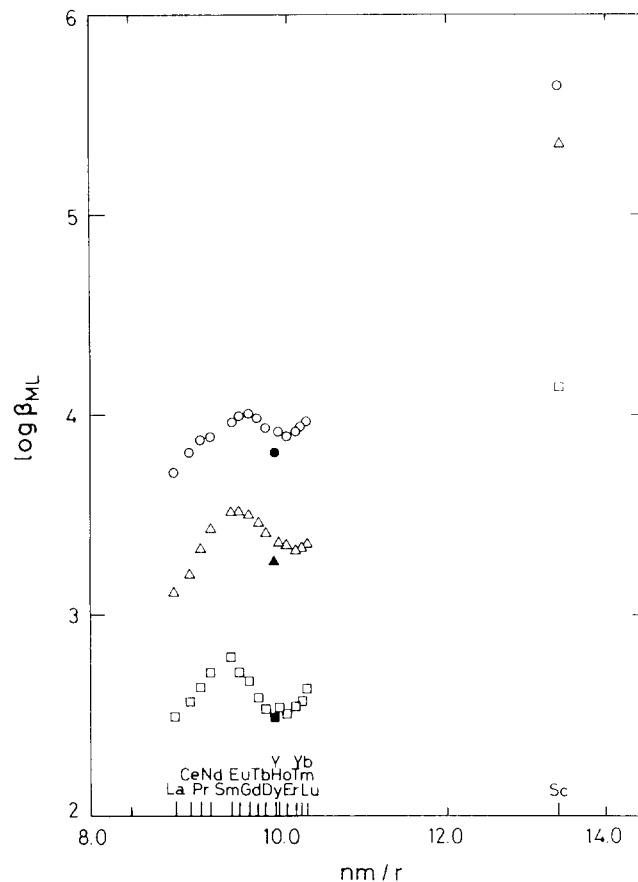


Fig. 3. Correlation between $\log \beta_{ML}$ and the reciprocal ionic radius (Sc^{3+} , CN 6; Y^{3+} , La^{3+} – Lu^{3+} , CN 8). \circ , citraconate; \square itaconate; \triangle mesaconate.

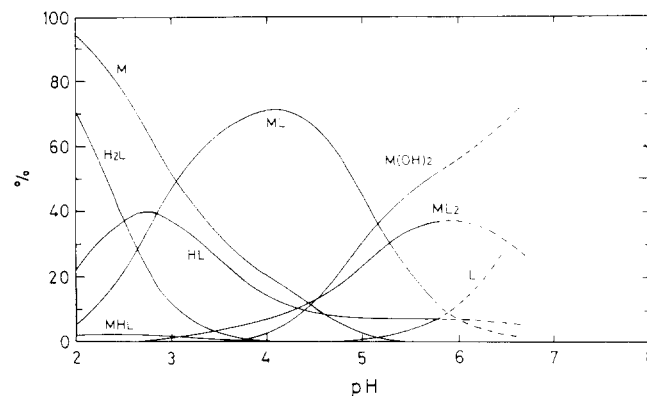


Fig. 4. Distribution of the species in a 1:1 molar ratio of citraconate to Sc^{3+} at 25.0 °C and at $I=0.1$ (KNO_3).

eight-coordinate for yttrium and lanthanides and six-coordinate for scandium [13], are shown in Fig. 3. Although it may not be reasonable to extrapolate the lines of the lanthanides as far as scandium, which apparently should have a lower coordination number than lanthanides, the stability constants of the scandium complexes with citraconate and itaconate ligands were close to the extrapolated lines of the corresponding

lighter rare earth complexes, rather than to those of the heavier rare earth complexes [6]; the constant for scandium mesaconate complex is not close to the extrapolated lines.

The species distribution of the scandium citraconate system is given in Fig. 4. The precipitates of scandium hydroxide or hydroxo complexes were formed above pH 5, where scandium hydroxide initiates the precipitation [14]. As mentioned earlier, the formation of the species $M(OH)_2$ could be expected from the calculation, although no direct information was available in solutions.

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