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Stability Constants of Scandium Complexes. I. Monocarboxylate Complexes Species

Hisako Itoh, Naomi Itoh, and Yasuo Suzuki*
Department of Industrial Chemistry, Faculty of Engineering, Meiji University,
Higashi-mita, Tama-ku, Kawasaki 214
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The stability constants of scandium complexes with some carboxylate ligands were determined potentiometrically at 25.0 and 40.0 °C and at an ionic strength of 0.10 with potassium nitrate as supporting electrolyte. The constants of the scandium complexes were appreciably greater than those of the corresponding lanthanoid complexes, as expected. The changes in free energy, enthalpy, and entropy for the formation of the scandium complexes were calculated from the stability constants at two temperatures.

Since scandium has a similar outer electron shell configuration to the trivalent lanthanoids, the chemical properties of scandium are close to those of the trivalent lanthanoids. The stability constants of various lanthanoid complexes have been determined by many investigators,[1] however, only a few investigations of scandium complexes have been reported so far. Trivalent scandium, which is the only oxidation state for scandium in solution, has a smaller ionic radius than any of the lanthanoids but is larger than that of aluminium.[2] Thus scandium(III) should form more stable complexes with both anionic and neutral ligands than the lanthanoids,[3] although it undergoes extensive hydrolysis in aqueous solution. In the present study, the stability constants of scandium complexes with some monobasic carboxylic acids were determined and compared with those of the corresponding lanthanoid complexes.

The method employed for determining constants was based on conventional potentiometry as developed by Bjerrum,[4] Sonesson,[5] and others, and has been used in the previous work[6,7] by one of the authours.

Experimental

Reagents. Scandium nitrate stock solution was prepared by dissolving scandium oxide of 99.9% purity in nitric acid and diluting to a definite volume with water. The concentration of excess nitric acid was as high as 0.035 mol dm^{-3} to prevent hydrolysis. The potasium nitrate stock solution was prepared from the purified salt. The buffer solution of each ligand acid was prepared by half neutralization of the acid solution with an appropriate amount of carbonate-free standard sodium hydroxide.

Apparatus. The pH of the sample solution was measured with an Orion model 701A digital pH/mV meter equipped with Orion Ross 810100 pH and 800500 double-junction reference electrodes. The instrument is capable of measuring pH of a solution with an accuracy of 0.001 unit.

Procedures. An aliquot portion of scandium nitrate solution was added to a volumetric flask together with a carboxylate buffer solution and potassium nitrate to bring the final solution to an ionic strength of 0.10. The flask was brought to the mark with water then suspended in a constant temperature bath set at 25.0 °C for 24 h. The sample solutions used in measuring acid dissociation constants were prepared in the same way as the sample solutions described above, but without scandium nitrate.

Results and Discussion

There have been no previous reports on the stability constants of scandium complexes with the ligand acids used in the present study, except for acetylacetone,[8] acetic acid,[9] and D-gluconic acid.[10] The stability constants of the scandium complexes obtained are shown in Table 1, along with the values from the previous work. The stability constants obtained are in good agreement with those of the previous work.

The relation between basicity of ligands and the stability constants of complexes has been extensively discussed.[11–16] The ligands of stronger basicity produce more stable complexes, in other words, ligands which strongly combine with protons form stable complexes with metal ions. The linear correlations between the basicity of a series of ligands and the stability constants of complexes have been reported.[11–16] The relation

Table 1. Logarithms of stability constants and thermodynamic data of scandium complexes at 25.0 °C and at $I=0.10$ (KNO_3)

Ligand acid	This work	Previous work	$-\Delta G$ / kJ mol^{-1}	$-\Delta H$ / kJ mol^{-1}	$T\Delta S$ / kJ mol^{-1}
α-Hydroxyisobutyric acid	4.84	—	27.6	115	−87.0
Isobutyric acid	4.47	—	25.5	90.1	−64.6
Glycolic acid	4.40	—	25.5	121	−96.2
Acetic acid	3.48	3.16[8]	19.6	1.25	18.8
Propionic acid	3.77	—	21.3	8.78	12.5
Mandelic acid	2.91	—	16.7	−5.43	22.1
D-Gluconic acid	4.21	3.92[9]	23.8	−52.3	76.5
Acetylacetone	7.77	8.88[7]	44.3	388	−344

between the stability constants of the scandium complexes and the basicity of the ligand acids used here is shown in Fig. 1. Isobutyric, acetic, and propionic acids do not have an alcoholic OH group, whereas α-hydroxyisobutyric, glycolic, mandelic, and D-gluconic acids have OH. In the latter acids, the OH group apparently contributes to form five-membered rings, consequently the stability constants are greater than those of the former.

In considering the ionic radius, it is expected that the greater the charge and smaller the ionic radius, the greater will be the stability of the complexes, since the energy of an ionic bond corresponds to the electrostatic work to bring metal ions close to ligands. The relationship to the stability constants of α-hydroxyisobutyrato, glycolato, gluconato, and mandelato complexes against ionic radius is shown in Fig. 2. The stability constants of scandium complexes are on the extrapolated lines of those of the lanthanoid complexes. In the case of the mandelato complexes, the gradient of the line is smaller than the others, possibly due to steric hindrance. The relations between the stability constants of isobutyrato, acetato, and propionato complexes and ionic radius are shown in Fig. 3. The scandium complexes are on the extrapolated lines of the lighter rare earth complexes rather than the heavier rare earth complexes. The previous investigations[17–21] indicated that the relation between the stability constants and ionic radii was remarkably different for each of the ligands studied, and that the trends in the stability of the rare earth complexes were dependent on the changes in the coordinating characteristics of the ligands as well as on the changes in the degree of cationic hydration. Therefore, the scandium complexes are thought to be similar to the lighter rare earth complexes with regard to the coordinating characteristics and the degree of cationic hydration.

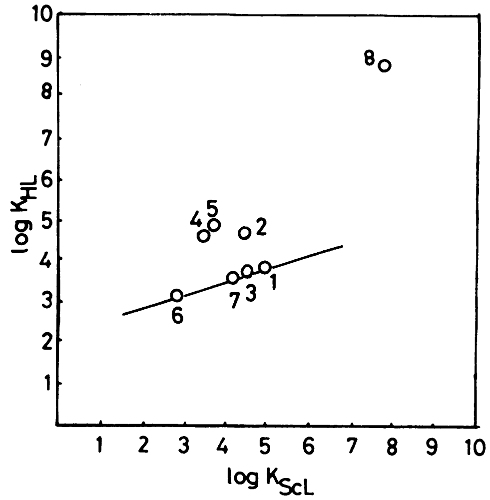

Fig. 1. Relation between stability constants of scandium complexes and basicity of ligands.
1: α-Hydroxyisobutyric acid, 2: isobutyric acid, 3: glycolic acid, 4: acetic acid, 5: propionic acid, 6: mandelic acid, 7: D-gluconic acid, 8: acetylacetone.

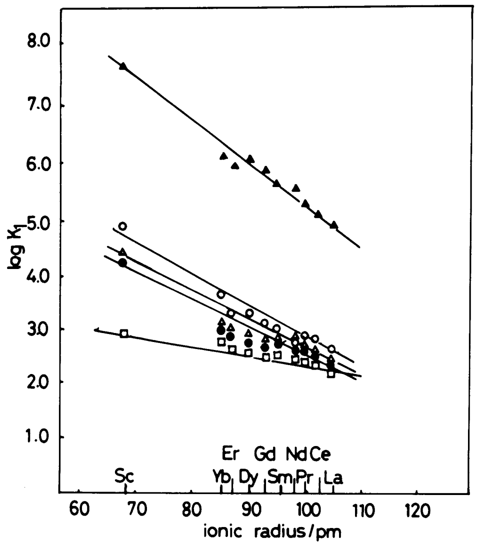

Fig. 2. Logarithms of stability constants of rare earth complexes. I.
○: α-Hydroxyisobutyrate, ●: D-gluconate, △: glycolate, ▲: acetylacetonate, □: mandelate.

The relation betweeen the stability constants of α-hydroxyisobutyrates and glycolates and ionization enthalpies of the rare earth elements are shown in Fig. 4. A straight line through yttrium, lanthanum, lutetium, and scandium, which have no d- and f-electrons, was obtained. Since electronegativity or ionization enthalpy is a measure of attracting electrons from the donor atoms of ligands, the linear relationships between the stability constants and the ionization enthalpy is reasonable. However, such lines were not obtained for isobutyrato, acetato, propionato, mandelato, gluconato, and acetylacetonato complexes.

The calculated values of the change in free energy, enthalpy, and entropy for the formation of the scandium complexes are shown in Table 1. Thermody-

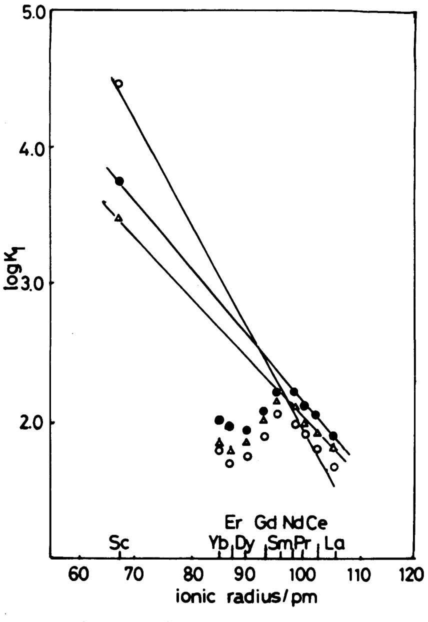

Fig. 3. Logarithms of stability constants of rare earth complexes. II.
○: Isobutyrate, ●: propionate, △: acetate.

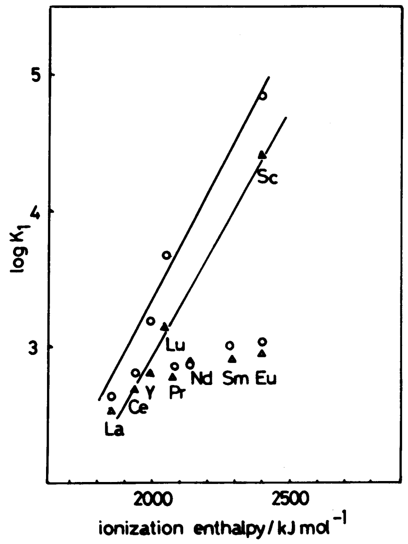

Fig. 4. Logarithms of stability constants of α-hydroxyisobutyrate and glycolate complex species *versus* ionization enthalpy.
○: α-Hydroxyisobutyrate, △: glycolate.

namic data on the scandium complexes indicate that $-\Delta H$ values are larger than $T\Delta S$ values for the α-hydroxyisobutyrate, isobutyrate, glycolate, and acetylacetonate systems. However, the entropy terms are larger than the enthalpy terms for acetato, propionato, mandelato, and gluconato complexes. The formation reactions of mandelato, and gluconato complexes are endothermic and the existence of the complexes is due to favorable entropy change. The increase in ΔS would be due to the increase in steric hindrance, thereby loosening the bond and increasing the configurational entropy of ligands such as mandelic and D-gluconic acids.

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