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Determination of Solubility Products of Rare Earth Fluorides by Fluoride Ion-selective Electrode

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Synopsis. Solubility product values of the rare earth fluorides were determined potentiometrically by using fluoride ion-selective electrodes at 25.0 °C. The $\mathrm{p}K_{\mathrm{sp}}$ values of the lanthanoid fluorides decreased gradually from 20.0 to 16.9, while the value for yttrium fluoride was locate in between those of terbium and dysprosium fluorides. The value for scandium fluoride was appreciably smaller than any of the lanthanoid fluorides, as expected from the cationic radii. The solubility product value of lanthanum fluoride single crystal could not be determined, since the saturated solution was not obtained through measurements of over three months.

Generally, the solubilities of lanthanoid salts increase with increasing atomic number when the anion of the salt arises from a strong acid and decreases with increasing atomic number when the anion originates from a weak acid. For example, solubility of the sulfates increases with increasing atomic number, while that of the hydroxides or dimethylphosphates decreases with increasing atomic number.[1)]

The solubility product values of lighter and heavier rare earth fluorides were determined titrimetrically by Nikolaev *et al.*[2)] and Ikurami *et al*,.[3)] respectively. Fraustro da Silva and Queimado[4)] also determined the solubility product values of the fluorides throughout the rare earth elements in mixed solutions of sodium fluoride and rare earth nitrates by using a fluoride ion-selective electrode. They showed that the solubility of the lanthanoid fluorides increased with increasing atomic number. In this study, the solubility product values of the rare earth fluorides, including yttrium and scandium fluorides, were determined in solution containing the respective fluorides only by using a fluoride ion-selective electrode.

Experimental

Reagents. Fifteen rare earth fluorides of 99.99% purity were obtained from Shin-etsu Chem. Ind. Co., Ltd. Single crystals of lanthanum fluoride prepared for the fluoride ion-selective electrode membrane were supplied from Denki Kagaku Keiki Co., Ltd. One of the single crystals was an europium-doped lanthanum fluoride. All the other chemicals were of reagent grade.

Apparatus and Procedure. Denki Kagaku Keiki model 7200 fluoride ion-selective electrode and model 4083 double junction Ag-AgCl reference electrode were used with Denki Kagaku Keiki model IOC-10 pH/mV meter.

A portion of a fluoride powder was taken into a covered polyethylene beaker together with water, and stirred continuously at 25.0 °C until a constant millivolt reading was obtained with the fluoride ion-selective electrode. After keeping the mixture for another day without stirring at 25.0 °C, an aliquot portion of the supernatant was brought to a pH of 5 with a portion of the Denki Kagaku Keiki pH5-AB buffer solution. To prevent the formation of hydrogen fluoride in acidic solutions, the sample solution has to be kept at pH 5 by using the buffer solution, as described above.

Calculations. In a solution, a rare earth fluoride should be dissociated as described in Eq. 1:

$$\mathrm{LnF_3} \longrightarrow \mathrm{Ln^{3+}} + 3\mathrm{F^-}, \tag{1}$$

where Ln means a rare earth element. The solubility product values can be calculated by Eq. 2, if no common ions are originally present in the solution:

$$K_{\mathrm{sp}} = [\mathrm{Ln^{3+}}][\mathrm{F^-}]^3 = \frac{[\mathrm{F^-}]^4}{3}. \tag{2}$$

Since the activity coefficient of fluoride ion may be considered unity in solution of such a low concentration, the activity of fluoride ion would be equal to the concentration.

Results and Discussion

The solubility product values obtained for the powder of the rare earth fluorides are shown in Table 1. The $\mathrm{p}K_{\mathrm{sp}}$ values apparently decrease with increasing atomic number of lanthanoids. This tendency agrees with the assumption that the solubility of the slightly soluble salts of lanthanoids derived from the anions of strong acids increases with increasing atomic number. On the other hand, one would expect that solubility decreases with increasing atomic number, since the size of the lanthanoid ion decreases and the lattice energy is inversely proportional to the sum of the anion and the cation radii. Fraustro da Silva and Queimado[4)] showed that the solubility product values would be affected by the lattice and hydration energies, and thus the order of the $\mathrm{p}K_{\mathrm{sp}}$ values was correct.

The comparison of the solubility product values of this study with the values of Fraustro da Silva and

Table 1. Solubility product values of rare earth fluorides

Fluoride	K_{sp}	$\mathrm{p}K_{\mathrm{sp}}$
$\mathrm{LaF_3}$	3.26×10^{-21}	20.5
$\mathrm{CeF_3}$	1.69×10^{-20}	19.8
$\mathrm{PrF_3}$	1.54×10^{-19}	18.8
$\mathrm{NdF_3}$	5.31×10^{-20}	19.3
$\mathrm{SmF_3}$	1.05×10^{-19}	19.0
$\mathrm{EuF_3}$	1.37×10^{-19}	18.9
$\mathrm{GdF_3}$	2.36×10^{-19}	18.6
$\mathrm{TbF_3}$	2.85×10^{-19}	18.5
$\mathrm{DyF_3}$	8.23×10^{-19}	18.1
$\mathrm{HoF_3}$	1.12×10^{-18}	18.0
$\mathrm{ErF_3}$	1.52×10^{-18}	17.8
$\mathrm{TmF_3}$	2.55×10^{-18}	17.6
$\mathrm{YbF_3}$	6.43×10^{-18}	17.2
$\mathrm{LuF_3}$	1.26×10^{-17}	16.9
$\mathrm{YF_3}$	4.41×10^{-19}	18.4
$\mathrm{ScF_3}$	2.98×10^{-12}	11.5

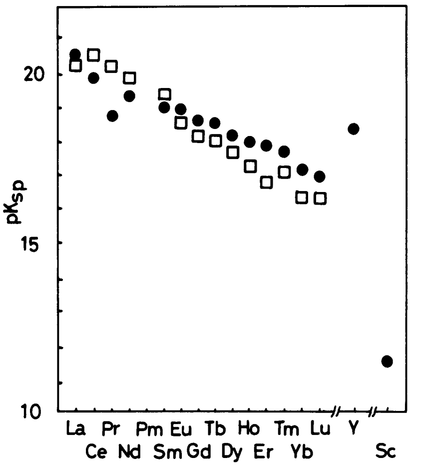

Fig. 1. A comparison of the pK_{sp} values of the rare earth fluorides at 25.0 °C.
●: This work, □: Fraustro da Silva and Queimado.[4]

Queimado is given in Fig. 1. Their report were made in mixed solutions of sodium fluoride and rare earth nitrate; thus the fluoride solutions contained nitrate, sodium, and rare earth ions. In this study, the solubility product values were determined by using the rare earth fluoride powder, and the sample solutions contained only rare earth and fluoride ions. As shown in Fig. 1, the present values are in fairly good agreement with those of Fraustro da Silva and Queimado, though the present pK_{sp} slope is apparently smaller than theirs. The rather unusual pK_{sp} location of praseodymium fluoride was not corrected even after the repeated measurements. The difference of the pK_{sp} values would be attributed to the origin of the rare earth fluorides present in the solutions.

The solubility product value of lanthanum fluoride single crystal was determined by the same experimental procedures as used for the powder fluorides; however, no saturated solutions of fluoride ion were obtained even after more than three months of continuous stirring. The previously reported solubility product values[5–8] of lanthanum fluoride single crystal were widely scattered and remarkably smaller than those of the powder fluorides, possibly because of the difference in crystal size or surface. Single crystals could be dissolved at considerably slower rates than the powder fluorides. This means that lanthanum fluoride single crystal is preferable to the fluoride powder as the fluoride ion-selective electrode membranes.

References

1) C. S. G. Phillips and R. J. P. Williams, "Inorganic Chemistry," Clarendon Press, Oxford (1966), Vol. 2, p. 112.

2) N. S. Nikolaev, Sh. A. Abdurakhmanov, and Kh. Sh. Dzhuraev, *Russ. J. Inorg. Chem.*, **19**, 618 (1974).

3) D. D. Ikurami, Kh. Sh. Dzhuraev, and N. S. Nikolaev, *Dokl. Akad. Nauk Tadzh. SSR*, **9**, 35 (1970).

4) J. R. Fraustro da Silva and M. M. Queimado, *Rev. Port. Quim.*, **15**, 29 (1973).

5) G. D. Moody and J. D. R. Thomas, "Selective Ion Sensitive Electrodes," Merrow, Watford (1971).

6) M. S. Frant and J. W. Ross, *Science*, **154**, 1553 (1966).

7) J. Buffle, N. Parthasarathy, and W. Haerdy, *Anal. Chim. Acta*, **68**, 253 (1974).

8) J. Vasely and K. Stulik, *Anal. Chim. Acta*, **73**, 157 (1974).