Methorics of the Precipitation Processes. XIII.
Study of the Precipitation of Sparingly Soluble Metal Fluorides*

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The precipitation processes of slightly soluble fluorides were studied tyndallometrically. In the case of CaF₂, MgF₂ and LaF₃ a crystallization maximum appeared in the accessible concentration region, while in the case of ThF₄ two maxima appeared which seemed to be the concentration and the isoelectric ones. The solubility products of the fluorides depended on the sol concentration.

INTRODUCTION

Among the salts of hydrofluoric acid those of calcium, magnesium, lanthanum and thorium are only slightly soluble in water. There was relatively little interest in fluorides before the World War II. As far as our problem is concerned, only a few authors reported their studies on the solid phase formation of CaF₂.¹⁻⁵ The interest increased during the war owing to the importance of fluorine chemistry in isolating nuclear fuel. Especially LaF₃ and ThF₄ became important, the first one as a carrier for the coprecipitation of heavy metals. Thus many studies on their crystal structure,⁶⁻⁷ radiochemistry⁸⁻⁹ and coprecipitation phenomena¹⁰⁻¹³ have been published since the war.

EXPERIMENTAL

CaF₂, MgF₂, LaF₃ and ThF₄ were prepared by the reaction

\[ \text{Me(NO₃)}_n + n\text{NH}_4\text{F} \rightarrow \text{MeF}_n \downarrow + n\text{NH}_4\text{NO}_3 \]

and the occurring precipitation process was investigated tyndallometrically while the sols were in statu nascendi¹⁴. Keeping the concentration of Me-ions constant within a series of systems, we varied the concentration of F-ions.

In the case of CaF₂ large maxima were obtained a little above the equivalence point i.e. in the region of F-ions excess (Fig. 1) when smaller concentrations of Ca-ions were used (1×10⁻² N and less), but the maxima were exactly at the equivalence point with larger concentrations of Ca-ions (e.g. 2×10⁻² N). The particles underwent a rapid growth, so that already within one minute the turbidities of the systems reached values which remained constant for several hours. Using the DQT method¹⁴ it was shown that the sizes of the particles were about 250 µm both at the maximum and in the neighbouring regions.

In the case of MgF₂ similar results were obtained. In this case the particles did not grow so rapidly, hence the 3-hours concentration tyndallograms are

shown (Fig. 2). Below the maxima there were regions of complete solubility which included also the equivalence points.

In the case of LaF$_3$ no true maxima were obtained (Fig. 3). Solid phase was formed above the equivalence point i.e. in the region of F-ions excess and no solid phase was formed below it i.e. in the region of La-ions excess. The limit between the regions of the solid phase formation and the solution, however, was not just at the equivalence point. At smaller La-ions concentrations ($1 \times 10^{-4} - 1 \times 10^{-2} \text{ N}$) it was shifted into the region of F-ion excess. At larger La-ions concentrations it was shifted on the other side of the equivalence point i.e. into the region of La-ions excess. The turbidities of these systems were very small when compared with those of CaF$_2$ and MgF$_2$. Also they underwent a much quicker sedimentation.

ThF$_4$ systems were the most interesting in the fluoride series. Their turbidities were very high even at smaller Th-ions concentrations (the work was done with $6 \times 10^{-3}$, $2 \times 10^{-3}$ and $5 \times 10^{-4} \text{ N}$). Two maxima were obtained with a minimum between them (Fig. 4). The first one had a constant lower limit at $1 \times 10^{-2} \text{ N}$ for F-ions concentration gradient, and the second one changed its position with changing the concentration of Th-ions and appeared always a little below the equivalence point i.e. in the region of Th-ions excess. The particles of the systems in the maxima grew very slowly but were very stable and did not undergo any remarkable sedimentation within 40 hours, whereas the systems in the minima underwent a quick sedimentation within several minutes. The sizes of the particles did not differ much in minima (shaken) and maxima, their average diameter being about 200 µm.

Such investigations on the fluoride series were carried on also with so small concentrations of Me-ions that no characteristic curves could be obtained but only the limits between the regions of solid phase formation and of the solution could be determined. If such limit points are plotted against the concentrations of Me-ions, the curves are obtained showing the areas of precipitation and of solubility (Fig. 5). From these data solubility products were estimated for the corresponding

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**Fig. 1.** Concentration tyndallogram of the system Ca(NO$_3$)$_2$ - NH$_4$F

**Fig. 2.** Concentration tyndallogram of the system Mg(NO$_3$)$_2$ - NH$_4$F
systems. It is shown in Table I that they differ from the data found in literature\textsuperscript{18} and that they are not constant but change their values with changing concentration of Me-ions, as it was shown also by Tarborg-Jensen\textsuperscript{3} for CaF\textsubscript{2}.

![Image 3](image3.png)

**Fig. 3.** Concentration tyndallogram of the system La(NO\textsubscript{3})\textsubscript{3} – NH\textsubscript{4}F

![Image 4](image4.png)

**Fig. 4.** Concentration tyndallogram of the system Th(NO\textsubscript{3})\textsubscript{4} – NH\textsubscript{4}F

![Image 5](image5.png)

**Fig. 5.** The areas of precipitation and solubilities of fluoride systems

Series of systems were prepared, also keeping the concentrations of F-ions constant and varying the concentration of Me-ions. At smaller F-ions concentrations (e.g. \(4 \times 10^{-4} \text{N}\) for ThF\textsubscript{4}, \(2 \times 10^{-2} \text{N}\) for MgF\textsubscript{2}) the maxima were again shifted a little above the equivalence point i.e. into the region of Me-ions excess. At
greater F-ions concentrations (e.g. $4 \times 10^{-2} N$ for MgF$_2$) the shift was in the other direction. In this case even LaF$_3$ showed a developed maximum.

As Tarborg-Jensen$^3$ and Bachmann and Pinnow$^2$ showed and de Boer and Dippel$^1$ explained, H-ions concentration influences the course of the precipitation of fluorides. In these investigations attention was paid to the pH estimation and the systems were found always slightly acid (pH 5.5—6.7) owing to the hydrolysis of Me(NO$_3$)$_n$ and NH$_4$F components.

**TABLE I**

*The Differences in Solubility Products of Fluorides as Found in the Literature and Obtained Experimentally.*

<table>
<thead>
<tr>
<th>Sol</th>
<th>Conc. Me$^{n+}$ (N)</th>
<th>$L$ exp.</th>
<th>$L$ lit.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ThF$_4$</td>
<td>6.0 x 10$^{-3}$</td>
<td>3.5 x 10$^{-14}$</td>
<td>2.8 x 10$^{-14}$</td>
</tr>
<tr>
<td>2.0 x 10$^{-3}$</td>
<td>3.3 x 10$^{-16}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0 x 10$^{-4}$</td>
<td>3.0 x 10$^{-19}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LaF$_3$</td>
<td>1.5 x 10$^{-2}$</td>
<td>1.1 x 10$^{-8}$</td>
<td>no data</td>
</tr>
<tr>
<td>7.4 x 10$^{-3}$</td>
<td>1.6 x 10$^{-9}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.7 x 10$^{-3}$</td>
<td>4.2 x 10$^{-10}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.8 x 10$^{-8}$</td>
<td>7.0 x 10$^{-11}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.4 x 10$^{-4}$</td>
<td>4.1 x 10$^{-11}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaF$_2$</td>
<td>2.0 x 10$^{-2}$</td>
<td>1.7 x 10$^{-8}$</td>
<td>5.2 x 10$^{-8}$</td>
</tr>
<tr>
<td>6.0 x 10$^{-3}$</td>
<td>1.9 x 10$^{-8}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0 x 10$^{-3}$</td>
<td>1.2 x 10$^{-8}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgF$_2$</td>
<td>2.0 x 10$^{-2}$</td>
<td>2.9 x 10$^{-6}$</td>
<td>7.3 x 10$^{-9}$</td>
</tr>
<tr>
<td>1.0 x 10$^{-2}$</td>
<td>2.4 x 10$^{-6}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0 x 10$^{-3}$</td>
<td>1.6 x 10$^{-6}$</td>
<td></td>
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</tr>
</tbody>
</table>

**DISCUSSION**

Owing to the solubilities of the reacting components and the precipitates formed, only a relatively narrow concentration region of solid phase formation could be investigated. Some precipitation phenomena, characteristic for other systems,$^{17}$ did, therefore, not appear.

In the accessible concentration region generally only one maximum was observed. In CaF$_2$ systems it appeared at the equivalence point when larger sol concentrations were used. This indicates its isoelectric character. Its shift, however, towards higher fluoride concentration with decreasing sol concentration indicates that it is a crystallisation maximum.$^{17}$

In MgF$_2$ systems the same situation was even more emphasized. The maxima were the crystallisation ones, shifting in the same way as those of CaF$_2$, and appearing always at the edge of the region of ionic solubility, which included also the equivalence point. The situation was similar in LaF$_3$ systems although no sharp maxima were obtained. A shift even into La-ions region was observed emphasizing the hypothesis of crystallisation maxima.
The character of \( \text{ThF}_4 \) maxima indicates that the first one is a concentration maximum with its lower limit (\( 1 \times 10^{-2} \text{N} \)) on F-ions gradient being the coagulation value of \( \text{ThF}_4 \) for monovalent counter-ions (\( \text{NH}_4^+ \)). The second, sharp maximum seems to be the isoelectric maximum of the \( \text{ThF}_4 \) system.

This shows that the precipitation phenomena are not governed only by the solubility factors but the specific characteristics of the stabilizing and crystal lattice building ions have to be considered. Not only do the solubility products (of fluorides) differ from the data found in literature, they are not even constants for a given salt but are functions of the sol concentration.

REFERENCES

IZVOD

Meteorika precipitacionih procesa. XIII.
Precipitacija teško topljivih fluorida metala.

B. Černicki and B. Težak

Procesi precipitacije slabo topljivih fluorida bili su praćeni tindalometrijski. Kod \( \text{CaF}_2, \text{MgF}_2 \) i \( \text{LaF}_3 \) pojavljuje se u pristupnom koncentracijskom području kristalizacioni maksimum, a kod \( \text{ThF}_4 \) pojavljuju se dva maksimuma, od kojih je jedan vjerovatno koncentracioni, a drugi isoelektrični. Produksi topljivosti fluorida ovise o koncentraciji sola.