Monatshefte für Chemie 126, 695–697 (1995)

Monatshefte für Chemie
Chemical Monthly

Short Communication

Zirconium-Phosphate-Fluoride Gels[†]

E. Fakhari and **T. Schönfeld***

Institute of Inorganic Chemistry, University of Vienna, A-1090 Wien, Austria

Summary. The volume of amorphous zirconium phosphate precipitates formed in acid solutions ($pH = 0$–2) is increased many times by the action of fluoride (hydrofluoric acid). At fluoride concentrations corresponding to a maximum precipitate volume, the particles slowly (during several days) coalesce to form a semi-solid gel.

Keywords. Fluoride ligands; Gels; Phosphate bridges; Polymeric zirconium cations; Zirconium phosphate; Zirconium-fluoride coordination.

Zirkonium-Phosphat-Fluorid-Gele (Kurze Mitt.)

Zusammenfassung. Das Volumen amorpher Zirkoniumphosphat-Niederschläge, die in saurer Lösung ($pH = 0$–2) erzeugt werden, vergrößert sich bei Einwirken von Fluorid (Flußsäure) auf ein Mehrfaches. Bei Fluoridkonzentrationen, die zu maximalem Niederschlagsvolumen führen, vereinigen sich die Niederschlagsteilchen langsam, d.h. innerhalb einiger Tage, unter Bildung eines gallertigen Gels.

Introduction

When fluoride (hydrofluoric acid) acts on amorphous zirconium phosphate which was precipitated from acid solutions ($pH = 0$–2) and consists of flocky, gelatinous particles, unexpected effects take place. Increasing the fluoride concentration leads to a considerable increase in volume of the settled precipitates, this change being observable within minutes. The precipitates which have the greatest volume due to action of fluoride may then change slowly, within 2 to 15 days, to a semi-solid gel, immobilized, for example, as a jelly-like plug on the bottom of a test tube. These effects were observed in connection with a study of the dissolution of zirconium phosphate by fluoride using radiotracer techniques [1].

Experimental and Results

The conditions under which the two effects occur are exemplified by the data for one of the experiments: An amorphous zirconium phosphate precipitate was first formed by mixing 2.0 ml of a zirconium

---

[†] Dedicated to Univ. Prof. Dr. *O. Olaj*, University of Vienna, on the occasion of his 60th birthday

Table 1. Influence of hydrofluoric acid on the volume of amorphous zirconium-phosphate precipitates; total concentrations of substances (key elements) in this series of experiments: $[Zr_t] = 0.010\,M$, $[P_t] = 0.0075\,M$, $[F_t] = 0\text{–}0.10\,M$, $[Na_t] = 0.38\text{–}0.48\,M$, $[Cl_t] = 0.46\text{–}0.56\,M$, $pH = 1.0$; total solution volume in each experiment: 10.0 ml; volume of settled precipitate in absence of hydrofluoric acid: $V_o = 1.0$ ml

$[F_t]/[Zr_t]$	0	0.5	1.0	2.0	4.0	6.0	10.0
V_F/V_o[a]	1.0	1.0	1.2	3.6[b]	2.1	1.7[c]	0.3[c]

[a] V_F/V_o: ratio of volume of layer of settled precipitate (after four days) in the presence of hydrofluoric acid to that in the absence of that substance; [b] formation of semi-solid gel; [c] formation of crystalline precipitate noticeable after four days

oxychloride solution (0.05 *M*, adjusted to *pH* 1.0 with $NaHCO_3$ and aged three weeks), 1.125 ml 1 *M* NaCl, 1.125 ml 0.2 *M* HCl, and 0.75 ml sodium phosphate (0.1 *M* Na_2HPO_4 adjusted to *pH* 1.0 with HCl). After aging this precipitate suspension (volume 5.0 ml) for one hour, 5.0 ml of a fluoride solution were added. This solution was a mixture of 2.0 ml 0.1 *M* NaF (adjusted to *pH* 1.0 with HCl), 2.5 ml 1.0 *M* NaCl, 0.3 ml 1.0 *M* HCl, and 0.2 ml H_2O. The mixture of the two solutions thus had the following overall composition, given in form of the total concentrations of key elements: $[Zr_t] = 0.010\,M$, $[P_t] = 0.0075\,M$, $[F_t] = 0.020\,M$, $[Na_t] = 0.40\,M$, $[Cl_t] = 0.47\,M$, $pH = 1.0$. The ratio of the amount of fluoride to that of zirconium, a quantity appropriate for discussing the effect of fluoride in these experiments, thus had the value $[F_t]/[Zr_t] = 2.0$.

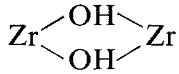
After settling for one hour, the flocky precipitate had a volume of 3.8 ml. Four days later the precipitate particles had coalesced to form a semi-solid gel with a volume of 3.6 ml. Carrying out the same experiment without addition of fluoride to the second solution, *i.e.* with $[F_t]/[Zr_t] = 0$, the volume of the precipitate was 1.5 ml after one hour and 1.0 ml after four days.

Results of a related series of experiments, in which several values of $[F_t]/[Zr_t]$ between 0 and 10 were investigated, with $[Zr_t]$ and $[P_t]$ being held constant, are shown in Table 1. From this and from other series of experiments of this kind, partly at different *pH* and $[P_t]/[Zr_t]$-values, it can be seen that increasing the fluoride concentration first causes an increase in precipitate volume, a maximum volume usually being found in the range $2 < [F_t]/[Zr_t] < 4$, whereas still higher fluoride concentrations lead to a strong decrease in volume. Gels are formed in samples for which the increase in volume shortly after adding fluoride is greatest. The volume ratios V_F/V_o (see Table 1) for these samples are in the range of 3.5 to 5.5.

Very similar results with regard to the volume of settled precipitates and gel formation are obtained if the order of mixing reagents is changed, *i.e.* if 5.0 ml of a solution containing zirconium, aged as indicated above, and fluoride is prepared first and this solution is then mixed one hour later with 5.0 ml of a solution containing phosphate, all solutions having been adjusted to the appropriate *pH* (in the range of 0–2). In these experiments, the amorphous zirconium phosphate is formed in the final mixing step.

Discussion

The great amount of solution held in the amorphous particles and in the gels should be noted. If the density of crystalline zirconium phosphate is taken to be $2.72\,g\cdot cm^{-3}$ (value for $Zr(HPO_4)_2$ [2]), the volume of solid in the precipitates described above is calculated to be about 0.010 ml. For the settled precipitates, an interstitial fraction of 0.3 can be assumed, giving a volume of precipitate particles in the absence of fluoride of about 0.7 ml. The volume of solid in the precipitate particles thus amounts to about 1.5% of the volume of the particles formed in the absence of fluoride and to about 0.4% of the volume of the gel formed when $[F_t]/[Zr_t] = 2$. The precipitate particles formed in the absence of fluoride, therefore, contain about 98.5% of solution by volume; the gel formed in the presence of fluoride contains about 99.6% solution.

The increase in volume due to hydrofluoric acid can be explained in the following way: In acid zirconium solutions ($pH = 0$–2) from which the amorphous zirconium phosphates were precipitated, zirconium is present in form of polymeric aggregates with  $\mathrm{Zr}\langle^{\mathrm{OH}}_{\mathrm{OH}}\rangle\mathrm{Zr}$ and Zr–O–Zr links [3, 4]. Precipitation takes places through phosphate ions forming bridging links (Zr–O–P–O–Zr) between the polymeric zirconium aggregates. As we have found in radiotracer experiments with ^{32}P, phosphate in the amorphous precipitates exchanges rapidly and nearly completely with phosphate ions in solutions, this rapid exchange being completed within minutes [1]. Thus, it is to be expected that ions with strong coordinating affinity to zirconium, such as fluoride, can substitute rapidly for phosphate ions in the amorphous precipitates with phosphate bridges between zirconium aggregates being broken in this way. The phosphate bridges are comparable to cross-links in organic polymers, *e.g.* in synthetic ion exchange resins. As the number of bridges between zirconium aggregates is reduced, the amorphous precipitates swell more readily and their volume grows.

The decrease in the volume ratio V_F/V_0 at high fluoride concentrations ($[F_t]/[Zr_t] \geqslant 4$) is due to zirconium phosphate being dissolved increasingly by destruction of more and more phosphate bridges between zirconium aggregates and formation of smaller zirconium polymeric ions with fluoride ions bound to zirconium atoms in the aggregates. Evidence for the formation of aggregates in which anionic ligands such as sulfate and fluoride are attached to polymeric zirconium cations was obtained in ion exchange experiments in which the behaviour of Zr and F was followed by radiotracers (^{95}Zr, ^{18}F) [5].

The slow gel formation is brought about by interdiffusion of zirconium phosphate aggregates between the primary precipitate particles. Due to the action of fluoride, *i.e.* the reduction in cross-linking, aggregates of reduced size, some of them possibly having linear form, are formed. Slow attack of fluoride on polymeric zirconium aggregates, which we have also observed in our experiments and which is based on the breaking of oxygen and hydroxyl bridges between zirconium atoms, is likely to be a contributing factor for the formation of smaller aggregates. The smaller aggregates will diffuse more easily and the increased diameter of the channels in the precipitate particles also facilitates the interdiffusion of aggregates. As indicated by the rapid phosphate exchange, there is a continuous breaking and establishing of phosphate bridges. The original precipitate particles can thus coalesce slowly by increased aggregate interdiffusion to form a semi-solid gel.

References

[1] Fakhari E (1991) Thesis, University of Vienna
[2] Clearfield A, Smith GD (1969) Inorg Chem **8**: 431
[3] Baes CF Jr, Mesmer RE (1976) The Hydrolysis of Cations. John Wiley, New York, pp 152–158
[4] Aberg M (1977) Acta Chem Scand A **31**: 171
[5] Fakhari E, Schönfeld T (1989) Monatsh Chem **120**: 1091

Received January 26, 1995. Accepted February 9, 1995