Potentiometric Study of Magnesium Fluoro Complexes in Aqueous Solutions up to 473 K and 1 kbar

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The formation of magnesium fluoro complexes in a hydrothermal fluorite-bearing model solution has been potentiometrically studied up to 473 K and 1 kbar at the ionic strength $I = 1$ m (NaCl), in order to estimate the competition with the formation of the lanthanide fluoro and fluorohydroxo complexes in such systems. No evidence of difluoro complex was found at p, T, $[F^-]$ and pH conditions which are relevant to fluorite formation. The apparent formation constant Q, as well as the apparent thermodynamic data ΔG, ΔS and ΔH of MgF^+ have been determined. The effect of pressure was found to be negligible. The competition with the lanthanide complexes becomes increasingly negligible with increasing T and in particular with increasing pH.

Key words: Formation of MgF^+ in hydrothermal fluorite-bearing solutions; Apparent thermodynamic data of MgF^+ at high p and T; Potentiometric study.

1. Introduction

The formation of magnesium fluoro complexes plays, in general, an important role in different geochemical systems. For instance, weakly acidic hydrothermal fluorite-bearing solutions (pH 3–6), contain Magnesium in a concentration of about 10^{-4} mol kg^{-1} (m). Richardson and Holland [1] studied the solubility of fluorite in $NaCl-CaCl_2-MgCl_2$ solutions and found it to be controlled by the common ion effect and by the presence of NaF, CaF^+ and in particular of MgF^+. They obtained the apparent formation constant (Q) of these complexes from the experimentally determined solubility quotient $(Q)_{CaF_2}$ of fluorite at different temperatures along with the corresponding saturation pressures and calculated the thermodynamic equilibrium constants (K) using an extended Debye-Hückel expression for the activity coefficients. Up to 333 K, the Q values could be obtained from the solubility data $[(Q_{MgF^+})_{333\,K} = 30.6 \pm 0.5\ m^{-1}$ at the ionic strength $I = 1$ m]. Their measurements at the next higher temperature (373 K) were not sensitive enough to give reliable values of Q. At 473 K and 533 K they extrapolated the values from curve fitting. Majer and Stulik [2] determined potentiometrically the apparent formation constants (β) of MgF^+ up to 358 K in 2 M $NaNO_3$ solution, using the fluoride membrane electrode $[(\beta_{MgF^+})_{358\,K} = 43.9\ m^{-1})]$.

The partition pattern of chemically similar trace elements in minerals, such as that of the lanthanides (Ln) in fluorite, is used as an indicator for revelation of the mineral genesis. Such a partition is mainly determined by the distribution equilibria of the trace elements between the mineral-bearing solution and the crystallizing mineral. Probable complexation of the trace elements in the solution controls the availability of the species suitable for co-precipitation with the mineral. In case of the lanthanides, their uncomplexed ions (Ln^{3+}) are the species that most probably have co-crystallized with hydrothermally formed fluorite. The typical fractionation between the light and the heavy members of the lanthanides, observed in their partition pattern in fluorite samples, is assumed to result from the different complexation degree within the series. Bilal and Langer [3] have, therefore, studied the complex formation of Ce^{3+}, Nd^{3+}, Tb^{3+}, Er^{3+} and Lu^{3+} by means of F^- and OH^- in 1 m NaCl solution under conditions relevant for the formation of hydrothermal fluorite (up to 473 K, 1 kbar and initial pH 3.6). They found that up to ≈333 K, the system is controlled by the formation of the monofluoro complexes. At higher temperature, OH^- participates increasingly in the complex formation process to form the monofluoro-monohydroxo complex which becomes obviously the most important one, determining the co-precipitation.

How far does the formation of magnesium fluoro complexes compete with that of the fluoro and fluorohydroxo complexes of the lanthanides in hydrother-

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mal fluorite-bearing solutions? The apparent formation constant of MgF^+ at 473 K and 1 kbar is expected to be $\leq 10^2\ m^{-1}$ which is by 9 orders of magnitude lower than that of (e.g.) $TbFOH^+$, determined in [3] under the same conditions. However, a competition of MgF^+ would be expected because of the high ratio of the total concentrations $C_{Mg^{2+}}/C_{Tb^{3+}} \approx 10^5$ estimated in hydrothermal fluorite bearing-solutions. This value results from the mol ratio* Ca/Tb $\approx 10^6$ found in fluorite that crystallized from solutions having the saturation Ca^{2+} concentration of $\approx 10^{-3}$ m and $C_{Mg^{2+}} \approx 10^{-4}$ m.

2. Experimental

$[F^-]$ was determined potentiometrically in the Cell

Reference electrode		Sample	Fluoride membrane electrode	
Ag/AgCl	NaCl (1 m)	NaF (x m) $MgCl_2$ (y m) pH = (z) $I = 1$ m (NaCl)	NaF (0.1 m) NaCl (0.1 m)	AgCl/Ag (1)
	diaphragm		LaF_3	

using the fluoride membrane electrode described previously by Bilal and Langer [4]. The measurements were carried out between 298 and 473 K in sets of solutions containing NaF in the concentrations $C_{F^-} = x = 1 \cdot 10^{-4}$, $2.5 \cdot 10^{-4}$, $5 \cdot 10^{-4}$, $6.75 \cdot 10^{-4}$, $1 \cdot 10^{-3}$, $2.5 \cdot 10^{-3}$, $5 \cdot 10^{-3}$ m, $MgCl_2$ in the concentrations $C_{Mg^{2+}} = y = 2.5 \cdot 10^{-3}$ and $5 \cdot 10^{-3}$ m and having the initial $(pH)_i = 3.3$, 3.5 and 3.8. The ionic strength was held constant at 1 m (NaCl). $[H^+]$ in every set was determined separately using the cell developed by Becker and Bilal [5] for high pressure–high temperature pH measurement. The needed values of the apparent association constant of HF (Q_{HF}) in the same medium have been determined previously by Becker and Bilal [6] up to 523 K and 1 kbar.

Argon was pressurized to the initial pressures $(p_i) = 31$ and 583 bar, which increased to 57 and 1020 bar, respectively, at 473 K. In case of pH measurements, the air in the autoclave was replaced by repeated pressurizing with pure hydrogen (99.999%) to $(p_i) = 31$ bar. Argon was then utilized for further pressurizing to the higher initial pressure.

No precipitation of MgF_2 was observed, even in the set with $x = y = 5 \cdot 10^{-3}$ m and $(pH)_i = 3.8$. Böttger [7] determined $10^{-8.19}\ M^3$ for the solubility product of MgF_2 at 300 K and $I = 0$ m. Assuming a maximum value of $[Mg^{2+}] \approx C_{Mg^{2+}}$ and taking the Q_{HF} values in [6] into account, $[Mg^{2+}][F^-]^2 \approx 10^{-7}\ m^3$ is estimated in this set at 298 K and 31 bar. Due to the common ion effect, obviously a higher value of the apparent solubility product results in 1 m NaCl solution. At higher temperature, $[F^-]$ and $[H^+]$ decrease due to the increased formation of HF. For instance, at pH = 4, 473 K and 57 bar, $\approx 10^{-8.98}\ m^3$ results for $[Mg^{2+}][F^-]^2$. However, the absence of precipitates during the potentiometric measurement in the autoclave was confirmed by the obtained potential curves as functions of T, which would have shown discontinuities at the beginning of precipitation.

Results and Discussion

A successive formation of Magnesium fluoro complexes is described by

$$(Mg^{2+})_{x(H_2O)} + i(F^-)_{y(H_2O)} \Leftrightarrow (MgF_i^{(2-i)+})_{z(H_2O)} + (x+y-z)\,H_2O, \quad (2)$$

$$[MgF_i]^{(2-i)+}/[Mg]^{2+}[F^-]^i = Q_i \quad (i = 1, 2). \quad (2a)$$

The mean ligand number $\tilde{n}$ is given by

$$\tilde{n} = \sum i Q_i [F^-]^i / (1 + \sum Q_i [F^-]^i. \quad (3)$$

$\tilde{n}$ is determined experimentally due to

$$\tilde{n} = (C_{F^-} - [F^-] - Q_{HF}[H^+][F^-]) / C_{Mg^{2+}}. \quad (4)$$

Figure 1 shows, as an example, $[F^-]$ (curves 1 and 2) and $[H^+]$ (curves 3 and 4) as functions of p and T in the solution with $(pH)_i = 3.5$, $C_{F^-} = 6.75 \cdot 10^{-4}$ m and $C_{Mg^{2+}} = 5 \cdot 10^{-3}$ m. Due to the increased formation of HF between 298 and 473 K, $[H^+]$ decreases approximately by a factor 0.24 in curve 3, but by a factor 0.35 in curve 4, because of the dissociation of HF with increasing pressure.

Equation (3) is valid, provided only mononuclear complexes are formed and no hydrolysis of Mg^{2+} takes place. The formation of polynuclear complexes was excluded by the fact that the determined $\tilde{n}$ values were independent of $C_{Mg^{2+}}$. In case of hydrolysis, the obtained $\tilde{n}$ values would be lower than the real ones. However, at the initial conditions, the hydrolysis needs not to be considered in all investigated solutions: Taking the values of the apparent ion product of water (Q_w) determined in 1 m NaCl by Becker and

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* The contents of the lanthanides are normalized to those found in Chondrites.

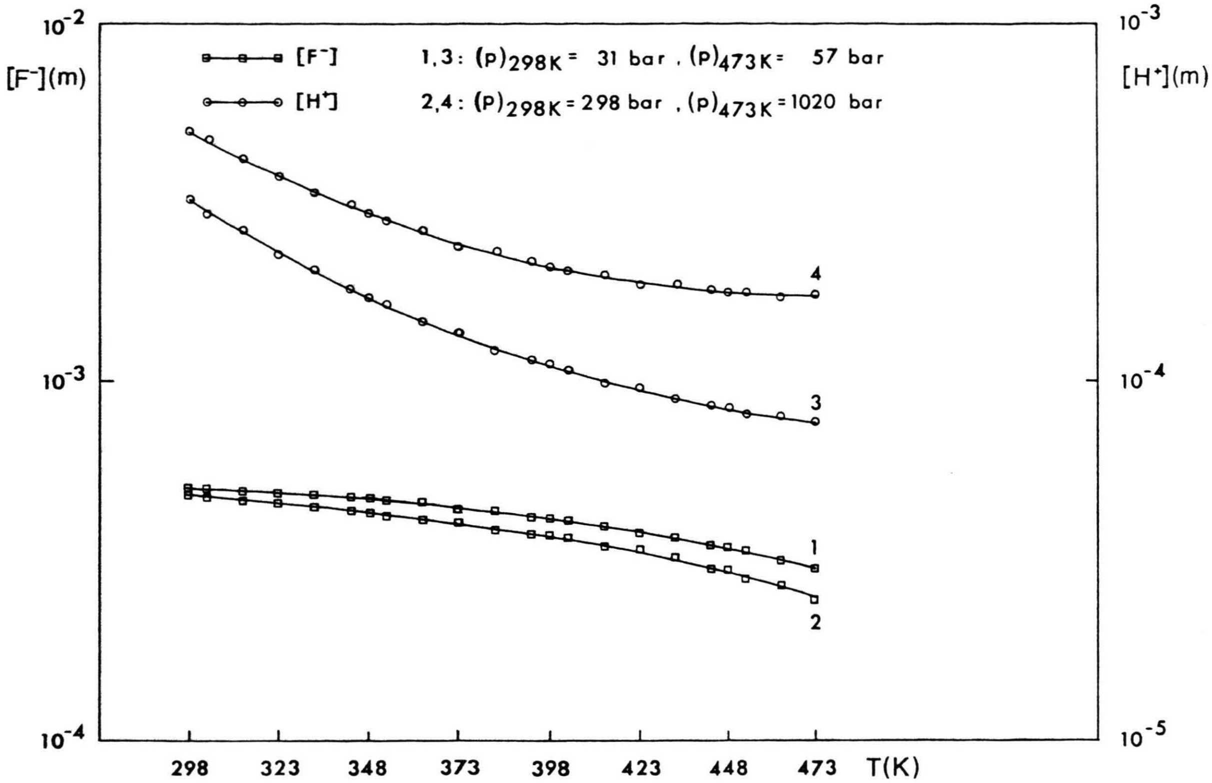

Fig. 1. $[F^-]$ and $[H^+]$ as functions of T at different pressures.

Bilal [8] into account, $[OH^-] \le 10^{-9.88}$ m is calculated. Using (for the first approximation) the formation constant $(K_{MgOH^+})_{298\,K,\,I=0\,m} = 10^{2.58}$ M^{-1} determined by Stock and Davies [9], and assuming no formation of other complexes, the ratio $[MgOH^+]/[Mg^{2+}] \approx 10^{-7.6}$ results. A lower value in 1 m NaCl medium is expected due to the lower apparent formation constant (Q_{MgOH^+}), so that the hydrolysis can surely be neglected.

Unfortunately, there are no data available for Q_{MgOH^+} at high p and T conditions. However, Kullgren [10] determined $\log Q_{MgOH^+} = 2.62$ at 373 K and $I = 0.18$ ($MgCl_2$). Kolthoff [11] determined $\log Q_{MgOH^+} = 2.4$ at 291 K in the same medium. Keeping in mind that only two values are available, $\log Q_{MgOH^+} \approx 2.8$ can be very roughly estimated at 473 K from a plot $\log Q$ vs. $1/T$, considering ΔH as constant. Taking $(Q_{HF})_{473\,K,\,57\,bar}$ in [6] and $(Q_w)_{473\,K,\,65\,bar}$ in [8] (the difference of Q_w due to $\Delta p = 8$ bar is relatively small), as well as $\log (Q_{MgF^+})_{473\,K} \approx 1.85$ estimated in [1] into account, the ratio $([MgOH^+]/[MgF^+])_{pH=4} \approx 0.06$ for the solution with the lowest $C_{F^-} = 10^{-4}$ m, respectively ≈ 0.0001 for that with the highest $C_{F^-} = 5 \cdot 10^{-3}$ m results. These values are supposed to be lower due to a smaller Q_{MgOH^+} expected in 1 m NaCl. However, the error in $\tilde{n}$ is relatively small. The $C_{MgH^{2+}}$ in (4) would be corrected by subtraction of $[MgOH^+] = Q_{MgOH^+}[Mg^{2+}][OH^-]$. Even if we (hypothetically) take $[Mg^{2+}] = 0.005$ m into account, $C_{Mg^{2+}}$ in (4) decreases by $\approx 10^{-6}$ m and leads to an error in $\tilde{n}$ of $\approx 0.02\%$, which is much less than the limit of experimental deviation.

Figure 2 shows the plots of the formation functions (3). The isothermal pressure increase leads to a slight decrease of $\tilde{n}$. The difference is within the limit of experimental deviation. It seems, therefore, that the pressure dependence of Q_i is negligible. The increase of $[F^-]$ at 473 K between the curves at 57 and 1020 bar (Fig. 1) is, therefore, mostly the consequence of the increasing dissociation of HF.

The change of th partial molal volume ΔV, which determines the isothermal pressure dependence of the free energy ΔG of reaction (2), results only due to the decreasing electrostriction of water accompanying the complex formation and is, therefore, relatively small. Thus, a volume contraction as a response to the pres-

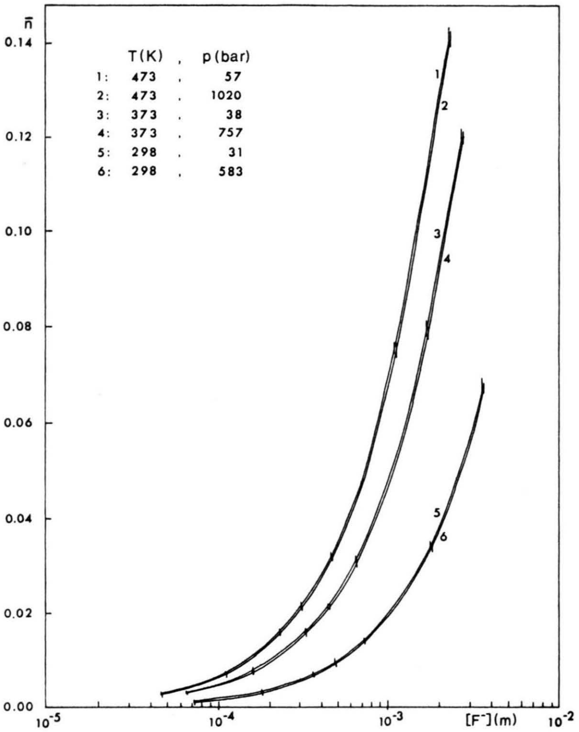

Fig. 2. $\tilde{n}$ as a function of $[F^-]$ at various T and p.

Table 1. Apparent thermodynamic data of reaction (1) at $I = 1$ m (NaCl) up to 473 K.

T (K)	Q_{MgF^+} (m^{-1})	ΔG (kJ mol^{-1})	ΔS (kJ mol^{-1})	ΔH (kJ mol^{-1})
298	19.8 ± 0.5	−7.38 ±	61.1 ±	10.82 ±
303	21.3 ± 0.4	−7.69 ±	60.9 ±	10.76 ±
313	25.3 ± 0.5	−8.39 ±	60.7 ±	10.61 ±
323	27.6 ± 0.5	−8.89 ±	60.5 ±	10.65 ±
333	31.1 ± 0.6	−9.50 ±	60.2 ±	10.59 ±
343	34.7 ± 0.5	−10.10 ±	59.8 ±	10.41 ±
348	37.9 ± 0.6	−10.50 ±	59.5 ±	10.21 ±
353	38.3 ± 0.7	−10.68 ±	59.0 ±	10.15 ±
363	44.6 ± 0.9	−11.44 ±	58.0 ±	9.61 ±
373	49.5 ± 1.1	−12.08 ±	57.0 ±	9.18 ±
383	51.1 ± 1.0	−12.51 ±	56.0 ±	8.94 ±
393	55.2 ± 1.2	−13.08 ±	55.5 ±	8.73 ±
403	57.8 ± 1.1	−13.57 ±	54.0 ±	8.19 ±
413	60.5 ± 1.3	−14.06 ±	52.5 ±	7.62 ±
423	62.2 ± 1.4	−14.51 ±	50.0 ±	6.64 ±
433	65.2 ± 1.6	−15.01 ±	46.5 ±	5.12 ±
443	66.5 ± 1.5	−15.43 ±	44.5 ±	4.28 ±
453	68.9 ± 2.1	−15.91 ±	42.5 ±	3.34 ±
463	70.1 ± 2.3	−16.33 ±	40.8 ±	2.56 ±
473	72.3 ± 2.5	−16.81 ±	39.0 ±	1.64 ±

sure increase must favour the increase of the ionic concentration in the system and lead to a slight dissociation of the complex.

The Q_i values are fitted from (3), which is rearranged to

$$Q_1 + Q_2[F^-](\tilde{n}-2)/(\tilde{n}-1) = \tilde{n}/\{(1-\tilde{n})[F^-]\}\,. \quad (5)$$

Only Q_i could be obtained from the fit, whereas no evidence for the formation of MgF_2 was found. Table 1 contains the apparent thermodynamic data of reaction (2) at the various temperatures. Due to the small decrease of the formation functions within a pressure increase of ≈0.5 kbar at 298 K, as well as ≈1 kbar at 473 K, the Q_1 values are considered to be nearly independent of p. The values given in [1] for $I = 1$ m at T up to 333 K are in good agreement with ours. Our average value at 473 K is ≈3% higher than that in [1], which is not unexpected due to the higher ionic strength ($I = 2$ m) used there. Elgquist [12] gave $(Q_1)_{298\,K} = 18.6 \pm 0.8$ M^{-1} at $I = 1$ M (NaCl). The small difference between this and our value seems to be due to the different scale of the ionic strength.

The partial differentiation of ΔG with respect to the pressure is considered to be zero. ΔS is, therefore, determined graphically from the slope of the plot ΔG vs. T, and ΔH is then calculated according to the fundamental equation. The ΔG, ΔS and ΔH values given in [1] are the standard ones and can, therefore, not be compared with ours. However, it is noteworthy to discuss, in particular ΔS ** in both cases, which is obtained due to

$$\Delta S^0 = S^0_{(MgF^+)\,c(H_2O)} + (a+b-c)\,S^0_{H_2O} - S^0_{(Mg^{2+})\,a(H_2O)} - S^0_{(F^-)\,b(H_2O)} \quad (6)$$

at infinite dilution, and in our case according to

$$\Delta S = S_{(MgF^+)\,z(H_2O)} + (x+y-z)\,S_{(H_2O)} - S_{(Mg^{2+})\,x(H_2O)} - S_{(F^-)\,y(H_2O)}\,, \quad (7)$$

where a, b and c are the hydration numbers at infinite dilution. We notice that i) both ΔS^0 and ΔS are positive, ii) $\Delta S^0 < \Delta S$ and iii) ΔS^0 increases with T, while ΔS decreases.

The first point is understandable due to the different degree of electrostriction of the water dipoles coordinated with the ions on both sides of reaction (2) ($i = 1$), since the electric field of Mg^{2+}, as well as that of F^-

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** We would like to draw the attention to a mistake done in the calculation of ΔH at 473 and 533 K reported in [1] due to an erroneous change of the sign of ΔS.

is higher than that of MgF^+ according to the higher charge and the smaller radius of Mg^{2+}, as well as the smaller radius of F^-.

Pure water (infinite dilution) has a much higher ordered structure than water containing electrolyte at $I = 1$ m (NaCl). The dielectric constant of water decreases, for instance at 294 K, from ≈ 70 at $I = 0$ M to ≈ 58 at $I = 1$ m (NaCl) due to the structure breaking effect of Na^+ and Cl^- ions resulting from their electrostatic interaction with the water dipoles. Unfortunately, neither the hydration numbers nor their variation with T are exactly known in both cases. However, if we assume $(a+b-c)$ to equal $(x+y-z)$, the second point is very probably due to the fact that on one hand $S^0_{H_2O} < S_{H_2O}$ and on the other hand $S^0_{(Mg^{2+})\,a(H_2O)}$, as well as $S^0_{(F^-)\,b(H_2O)}$ are respectively $< S_{(Mg^{2+})\,x(H_2O)}$ and $= S_{(F^-)\,y(H_2O)}$ because of the electrostatic interaction of the coordinated water with the ions of the background electrolyte. Obviously, due to the already existing lower order of the coordination sphere around MgF^+ (because of the lower electric field), the entropy of this hydrated ion decreases to a smaller degree than that of the hydrated Mg^{2+} and F^- when going from infinite dilution to 1 m NaCl solution.

The ordered structure of pure water transists increasingly to the monomeric structure with increasing T. In presence of electrolyte, such as NaCl, the transition takes more rapidly place and the self dissociation of water occurs to a higher rate. This leads to a much smaller decrease of $S^0_{H_2O}$ at a given T than that of S_{H_2O}. Furthermore, with increasing T the orientation of the coordinated water dipoles, particularly of those coordinated with Mg^{2+} and F^-, decreases more strongly in presence of electrolyte than at infinite dilution. This would very probably explain the third point.

According to the solubility data determined in [1] at 373 and 473 K under saturation pressure in 1 m NaCl, fluorite-bearing solutions are supposed to have the total fluoride concentration $(C_{F^-})_{373\,K} \approx 1.8 \cdot 10^{-3}$, $1.3 \cdot 10^{-3}$, $1.26 \cdot 10^{-3}$ and $1.2 \cdot 10^{-3}$ m, as well as $(C_{F^-})_{473\,K} \approx 2.2 \cdot 10^{-3}$, $1.5 \cdot 10^{-3}$, $1.36 \cdot 10^{-3}$ and $1.3 \cdot 10^{-3}$ m at pH 3, 4, 5, and 6, respectively. Due to the relatively small pressure effect observed, in general, on solubility equilibria (if no gas components are involved), these values are considered to be approximately valid at 1 kbar too. According to the (Q_w) values given (respectively approximated from the plot $-\log Q_w$ vs. p at different T) in [8], $[OH^-]_{373\,K,\,1\,kbar} \approx 10^{-7.96}$, $10^{-6.96}$, $10^{-5.96}$ and $10^{-4.96}$ m as well as $[OH^-]_{473\,K,\,1\,kbar} \approx 10^{-7.26}$, $10^{-6.26}$, $10^{-5.26}$ and $10^{-4.26}$ m are respectively calculated at these pH values. Taking, for instance, the apparent formation constants of terbium complexes determined in [3] at 373 K and 1 kbar $[(\beta_{1,0})_{TbF^{2+}} = 10^{3.54}$ and $(\beta_{1,1})_{TbFOH^+} = 10^{11.43}]$ and at 473 K and 1 kbar $[(\beta_{1,0})_{TbF^{2+}} = 10^{3.6}$ and $(\beta_{1,1})_{TbFOH^+} = 10^{11.1}]$, as well as the $(Q_{MgF^+})_{473\,K,\,1\,kbar} = 72 \pm 5.1\ m^{-1}$ into account, the $[MgF^+]/[TbFOH^+]$ ratios in Table 2 result from

$$C_{Tb^{3+}} = [Tb^{3+}]\,(1 + \beta_{1,0}[F^-] + \beta_{1,1}[F^-][OH^-])\,, \quad (8)$$

$$[MgF^+]/[F^-] = Q_1\,C_{Mg^{2+}}/\{1 + Q_1\,C_{F^-}/(1 + Q_{HF}[H^+])\}\,, \quad (9)$$

$$[TbFOH^+]/[F^-] = \beta_{1,1}[OH^-]\,C_{Tb}/\{1 + \beta_{1,0}\,C_{F^-}/(1 + Q\,HF\,[H^+]) + \beta_{1,1}[OH^-]\,C_{F^-}/(1 + Q_{HF}[H^+])\}\,. \quad (10)$$

Table 2. Approximate ratios of $[MgF^+]/[TbFOH^+]$ in fluoride-bearing solutions at 373 K, 473 K, 1 kbar and pH 3, 4, 5, and 6.

373 K				473 K			
pH 3	pH 4	pH 5	pH 6	pH 3	pH 4	pH 5	pH 6
354	4.2	0.04	0.0004	263	1.42	0.01	0.0001

The competition of the formation of the magnesium fluoro complex with that of the fluoro and fluorohydroxo complexes of the lanthanides become increasingly negligible with increasing temperature, and in particular with increasing pH.

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