KINETICS OF DISSOLUTION OF THE ALKALINE EARTH FLUORIDES

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ABSTRACT

Constant composition technique have been used to study the dissolution of the fluorides of magnesium calcium, strontium and barium in aqueous solution at an ionic strength of 0.15 M, as a function of concentration temperature and fluid dynamics. The method enables kinetic data to be obtained at very low undersaturation with a precision hitherto unobtainable. With the exception of magnesium fluoride, a striking change in the mechanism of dissolution is observed as the driving force is changed. At higher driving force the first order dependance of the rate of dissolution on the undersaturation suggests the diffusion controlled process normally assumed for dissolution reactions. At low driving force, however, the effective order of reaction appears to approach the value of 2, proposed for a surface controlled reaction. The rate of dissolution mol. min^{-1}. m^{-2} increases dramatically from Magnesium fluoride to Barium fluoride. The results can be interpreted in the light of the stability constants, lattice energy, thermodynamic parameters and dehydration of cations.

INTRODUCTION

The dissolution of alkaline earth fluoride is of importance in view of its use as a primary source of fluorine and also as single crystals in optical devices. Biologically, the topical application of fluoride solutions to tooth enamel results in a partial transformation hydroxyapatite to fluorapatite on the anamel surface, resulting in a much more caries-resistant phase. At higher concentrations of the fluoride ion, calcium fluoride forms at the tooth surface in addition to fluorapatite. The inhibition of dental caries that results from the topical application of fluoride salts has been related

to a surface coating of calcium fluoride on enamel which protects the mineral phase, hydroxyapatite, from dissolution, to reduce dental caries.

Little is known concerning the crystal growth and dissolution of alkaline earth fluorides. In order to clarify the rate and mechanism of the dissolution of the alkaline earth fluorides, a constant composition method [1] has been used under conditions of constant temperature, ionic strength and undersatuartion. The undersaturation was maintained constant during the reaction by the addition of potassium nitrate solution (medium electrolyte) controlled by a specific fluoride ion electrode. This method could be used to study the rates of dissolution at very low undersaturation.

EXPERIMENTAL

Undersaturation solution of the alkaline earth fluoride were prepared using both ultrapure (Alfa Chemicals) and reagentgrade (J.T. Baker) chemicals with triply distilled deionized water. Metal ion concentrations were determined by atomic absorption or by exchanging of hydrogen ion on a Dowex-50 ion exchange resin and titrating the liberated acid with standard potassium hydroxide. All fluoride solutions were prepared and stored pin polyethlene or polypropylene bottels in order to prevent fluoride attack on glass surfaces.

Seed crystals of the alkaline earth fluorides were prepared by precipitation, mixed potassium fluoride solution with metal nitrate solution at 25°C. The precipitations were made in polyethylene containers in a nitrogen atmosphere in order to eliminate the possibility of carbonate formation. The seeds were washed with saturated solutions of the metal fluorides and allowed to age for at least one month at 25°C, until the specific surface area reached a constant value. Seed crystal structure was confirmed by X-ray powder diffraction (Phillips XRG 3000 X-ray diffractometer, Ni filter and Cu/K radiation), and their morphology was determined by scanning electron microscopy (ISI Model II scanning electron microscope); specific surface areas, (SSA), were measured by a single point BET nitrogen absorption apparatus using 30% nitrogen nitrogen/helium mixture (Quantasorb II, quantachrome, Greenvale, N.Y.). Details of the seed crystals are given in Table 1.

Dissolution experiments were made in a 300 ml pyrex double-wallled reaction cell filled with a Teflon lid and polyethylene liner, maintained at constant temperature ($\pm$ 0.1°C) and stirred with a magnetic stirrer. Nitrogen gas was bubbled continuously through the solutions during the experiments. At the beginning of each experiment, the fluoride electrode was standarized by adding aliquots of potassium fluoride solution to the back ground potassium nitrate solution in the cell. Subsequently, undersaturated solutions of any desired concentration were prepared by the slow addition of metal nitrate solution. Following the introduction of metal fluoride seed crystals, the activities of ion species were maintained

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TABLE 1

Metal Fluoride seed crystals.

Salt	Mean Diameter μM	Specific surface area m^2g^{-1}	Solubility Products ($mol^3 L^{-3}$) at 25°C		ref
Magnesium fluoride	0.5	7.2	MgF_2 (s) ⟶ Mg^{2+} + $2F^-$	8.52×10^{-9}	3
Calcium fluoride	0.8	2.3	CaF_2 (s) ⟶ Ca^{2+} + $2F^-$	2.85×10^{-11}	3
Strontium fluoride	0.1	36.5	SrF_2 (s) ⟶ Sr^{2+} + $2F^-$	2.45×10^{-9}	19
Barium fluoride	1.5	0.5	BaF_2 (s) ⟶ Ba^{2+} + $2F^-$	1.40×10^{-2}	20

constant by the addition of potassium nitrate as diluent controlled by means of a pH-stat (Metrohm combirator model 3D, Brinkman Instrument Co.) using a fluoride specific electrode (Orion model 94–09), coupled with a thermalelectrolytic silver, silver chloride reference electrode. This reference electrode was designed to include an intermediate liquid junction containing background electrolyte so as to eliminate errirs due to leakage of salt bridge solution into the dissolution cell during the reactions. The reference electrode limb which was immersed in the cell solution was constructed of Teflon. Periodically, aliquots, of reaction mixture were withdrawn, and filtered (0.22 um Millipore). The filtrate was analysed for metals by atomatic absorption (Perkin Elmer Model 503) in order to verify the constancy of the concentrations ($\pm$ 1.0%). The solid phases collected during the experiment were investigated by X-ray diffraction, and by scanning electron microscopy (IS I Model II).

RESULTS AND DISCUSSION

To analyze the kinetics of the dissolution reactions of alkaline earth fluoride, it is necessary to take into account electroneutrality and the thermodynamic equilibrium constants, K, for the various associated species in the equilibria:

HF	$\longrightarrow$	H^+	$+$	F^-	6.61×10^{-4},	ref (2)
HF^-_2	$\longrightarrow$	HF	$+$	F^-	0.295	ref (2)
MgF^+	$\longrightarrow$	Mg^{2+}	$+$	F^-	0.93×10^{-3},	ref (3)
$MgOH^+$	$\longrightarrow$	Mg^{2+}	$+$	OH^-	2.63×10^{-3},	ref (4)
CaF^+	$\longrightarrow$	Ca^{2+}	$+$	F^-	9.12×10^{-2},	ref (5)
$CaOH^+$	$\longrightarrow$	Ca^{2+}	$+$	OH^-	4.27×10^{-2}	ref (6)
SrF^+	$\longrightarrow$	Sr^{2+}	$+$	F^-	0.147 ,	ref (5)
$SrOH^-$	$\longrightarrow$	Sr^{2+}	$+$	OH^-	0.150 ,	ref (6)
BaF^+	$\longrightarrow$	Ba^{2+}	$+$	F^-	0.357 ,	ref (5)
$BaOH^+$	$\longrightarrow$	Ba^{2+}	$+$	OH^-	0.227 ,	ref (3)

The computations were made by successive approximations for the ionic strength, I, as described previously[7] using activity coefficients calculated from the extended form of the Debye-Huchkel equation proposed by Davies.[8] The themodynamic solubility products, K_{SO}, for the alkaline earth metal fluoride are given in Table 1, together with SSA of the seed crystals.

Concentrations of ionic species in the undersaturated solutions were calculated as described previously[9]. The undersaturation, 0 , may be expressed.

<center>TABLE 2</center>
<center>Dissolution Kinetics of the alkaline earth fluoride at 25°C.</center>

	o 10^2	T_M (10^3 mol^{-1})	rate $(\text{mol min}^{-1}\text{m}^{-2})$	$(\text{rate} / o^{\,n})$	K (m s^{-1})
MgF_2	50	1.04	6.30×10^{-8}	1.26×10^{-11}	4.13×10^{-18}
	60	0.83	1.18×10^{-7}	1.95×10^{-11}	6.40×10^{-18}
	65	0.73	1.59×10^{-7}	2.45×10^{-11}	8.04×10^{-18}
	70	0.63	2.04×10^{-7}	2.91×10^{-11}	9.55×10^{-18}
	75	0.52	3.30×10^{-7}	4.40×10^{-11}	1.44×10^{-17}
	80	0.42	6.51×10^{-7}	8.14×10^{-11}	2.67×10^{-17}
				3.52×10^{-11}	1.15×10^{-17}
CaF_2	7.5	0.178	8.98×10^{-8}	1.20×10^{-8}	4.91×10^{-15}
	10	0.173	3.86×10^{-7}	3.86×10^{-8}	1.58×10^{-14}
	15	0.164	0.02×10^{-7}	5.35×10^{-8}	2.19×10^{-14}
	20	0.154	1.47×10^{-6}	7.35×10^{-8}	3.00×10^{-14}
				4.44×10^{-8}	1.52×10^{-14}
SrF_2	0.75	1.464	7.30×10^{-7}	9.73×10^{-7}	4.82×10^{-13}
	1.00	1.460	1.45×10^{-6}	1.45×10^{-6}	7.18×10^{-13}
	1.25	1.457	2.13×10^{-6}	1.70×10^{-6}	8.42×10^{-13}
	1.50	1.453	2.91×10^{-6}	1.94×10^{-6}	9.61×10^{-13}
				1.52×10^{-6}	7.51×10^{-13}
BaF_2	8	13.968	4.78×10^{-4}	5.98×10^{-5}	3.57×10^{-11}
	10	13.665	7.28×10^{-4}	7.28×10^{-5}	4.34×10^{-11}
	12	13.361	1.07×10^{-3}	8.92×10^{-5}	5.32×10^{-11}
				7.39×10^{-5}	4.41×10^{-11}

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$$O = [([M^{2+}]_o [F^-]_o^2)^{1/3} - ([M^{2+}] [F^-]^2)^{1/3} /([M^{2+}]_o [F]_o^2)^{1/3} \quad (1)$$

where $[M^{2+}]$, $[F^-]$ and $[M^{2+}]_o$, $[F^-]_o$ are the concentrations of lattice ions at time t and at equilibrium, respectively. The latter values were calculated from conditions of solubility products at the used ionic strengths. For the most soluble salt studied, barium fluoride, it was neassary to use relatively high ionic strength (0.43 mol L^{-1}) and conditional equilibrium costants were valid only at this ionic strength, since the use of an extended Debye-Huckel equation under these conditions is unjustified.

The results of the dissolution experiments are summarized in Table 2 together with the initial concentartions of metal ion, ionic strength, the range of under saturation, O , used in experiments and the rates of dissolution as given by the equation.[10]

$$\text{rate} = R = d(M_a A_b)/ dt = K_D S K_{so} n/v \quad o^n = K,S o^n \quad (2)$$

where K' is a constant, K_D is the rate constant for dissolution, S is a function of the initial seed surface area, K_{so} is the solubility product at the ionic strength of the experiment, v is the number of ions of electrolyte and n is the effective order of reaction.

The orders of reaction, n, for each of the salts were for MgF_2, n = 3.50 $\pm$ 0.15 (for $0.25 < o < 0.75$); for CaF_2, n= 1.00 $\pm$ 002 (for $0.24 < o < 0.40$) and n = 1.93 $\pm$ 0.07 (for $0.075 < o < 0.20$) and $\bar{n}$ = 1.93 $\pm$ 0.10 (for $0.0075 < o < 0.0150$) and for BaF_2. n = 1.0 $\pm$ 0.2 (for $0.15 < o < 0.20$) and n = 2.0 $\pm$ 0.2 (for $0.08 < o < 0.12$).

Thd rate of dissolution of crystals in an aqueous suspension is in general[11-16] either controlled by surface processes, or by the transport of substance between the volume adjacent to the dissolving surface and the bulk solution or by a combination of such processes. In order to compare the dissolution rates for different electrolytes, the comparison must be limited to substance which dissolve by similar mechanism at a given temperature. The experimental dissolution parameters should be normalized with respect to undersaturation and the active unit surface area. The normalized rate of dissolution may be represented by the value of $K' = \text{rate}/S o^n$, the values of n should also be the same within experimental error. Normalization of seed surface are made by comparing rates of dissolution per unit seed surface area and expressed as mol $min^{-1} m^{-2}$. As shown in table 2 the rate of dissolution changes dramatically from BaF_2 to MgF_2 in the same order of solubility changing (i.e. $MgF_2 < CaF_2 < SrF_2 < BaF_2$). Many physical properties of the fluorides of the alkaline earth metals has the same trend as more evendence for kinetic results.

The adsorption coefficient for contact adsorpation of the partially dehydrate ions at the crystal surface has discussed[19] in order to calculate absolute linear rate constants K (ms^{-1}). The calculated values for the rate

TABLE 3
Rate constants (K_{ex}) for the dehydration of alkaline earth
cations, and calculated ($K_{calc.}$) and experimental (K_{exp}) dissolution
rate constants of alkaline earth fluoride.

Salt	K_{ex} (s^{-1})	K_{calc} (ms^{-1})	K_{exp} (ms^{-1})
MgF$_2$	5.0 x 10^4	3.8 x 10^{-6}	1.2 x 10^{-18}
CaF$_2$	1.6 x 10^8	9.9 x 10^{-5}	1.8 x 10^{-14}
SrF$_2$	5.0 x 10^8	1.6 x 10^{-3}	7.5 x 10^{-13}
BaF$_2$	1.6 x 10^9	3.9 x 10^{-2}	4.4 x 10^{-11}

constants are summarized in Table 4. The experimental effective linear
dissolution rate constants, K (ms^{-1}), may be calculated by means of equation
3:

$$K = K'M / \rho \quad , \quad (6 \times 10^7) \qquad (3)$$

in which ρ is the crystal density expressed in g cm^{-3} and M represents the
molecular weight in g mol^{-1} [20] Equ. (3) is valid only for cubic or spherical
crystals which dissolve uniformly.[21] Microscopic examination of the

TABLE 4
Activation energy, Lattice energy and
energy of dehydration of Alkaline earth Fluorides.

	MgF$_2$	CaF$_2$	SrF$_2$	BaF$_2$
G^*_w/ 10^{-21}J	77	43	39	34
Lattice energy (KCal/mole)	695	624	588	-
E (KJ/mole)	71.13	62.24	-	25.59

cubic crystals during the growth experiments confirmed a predominantly uniform dissolution.

It can be seen from Table 4 that there is a general parallelism between K_{exp} and K_{cal}.

The higher values of activation energies for dissolution, activation energies for release of a water molecule from the hydration shell and lattice energy for magnesium fluoride compared with others fluorides Table 3 can explain the much lower experimental dissolution rate of magnesium fluoride.

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