The dissolution and growth of sparingly soluble inorganic salts: A kinetics and surface energy approach

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Abstract: This paper examines the role of interfacial free energy, especially the electron acceptor/donor or Lewis acid-base (AB) terms, in regulating not only the rates of these reactions but also in determining the solubility behavior of the crystal, S_∞. For a considerable number of compounds, the solubilities show a general increase as the solid/liquid interfacial tensions (γ_{SL}) decrease, but despite suggestions to the contrary, the relationship between γ_{SL} and $\log S_\infty$ should not necessarily be linear. Interfacial tensions between water and the solid surfaces of a number of sparingly soluble electrolytes have been determined by contact angle measurements by using surface tension component theory to yield the Lifshitz-van der Waals (LW) and Lewis acid-base components. The systems to be discussed will include dicalcium phosphate dihydrate (DCPD), octacalcium phosphate (OCP), hydroxyapatite (HAP), and fluorapatite (FAP). The interfacial tension values, -4.2, 4.3, 10.0, and 18.5 mJ m^{-2}, respectively, were of the same order of magnitude as those calculated from crystallization and dissolution kinetics data.

INTRODUCTION

In terms of chemical equilibrium, solubility is simply the amount of dissolved solute contained in a saturated solution when particles of solute are continually passing into solution (dissolving) while other particles are returning to the solid solute phase (growth) at exactly the same rate. Crystal growth, dissolution and solubility, three important processes for a solid solute in solution, are closely related to each other. Crystallization and dissolution kinetics express the net rate of reaction with respect to the solubility state. Their quantification must be based on reliable experimental information concerning factors controlling the dissolution, formation and transformation of crystals. It is important to note that interfacial free energies must also be involved in these processes but unfortunately, they are usually ignored in conventional kinetic approaches.

Calcium phosphates are some of the most common and widely dispersed minerals in nature, and they have been extensively studied from a solution chemistry point of view. Brushite ($CaHPO_4 \bullet H_2O$, DCPD) and octacalcium phosphate [$Ca_8H_2(PO_4)_6 \bullet 5H_2O$, OCP] are much more soluble than hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$, HAP]. Both are formed very readily due to their relatively rapid crystal growth rates, and they are found in many circumstances where they are metastable with respect to the thermodynamically more stable HAP, serving as precursor phases. In the laboratory, it is quite common to find that DCPD or OCP form initially followed by the more stable salts, either by hydrolysis in situ, as is probably the case in the transition from OCP to HAP, or through stepwise dissolution and reprecipitation, as seems to be the case in the conversion of brushite into other, more stable forms. Substitution of fluoride for hydroxide in HAP results in the formation of a more stable fluorapatite [$Ca_{10}(PO_4)_6F_2$, FAP] which is an important phase in the reaction of enamel surfaces with fluoride ion during topical fluoride treatment of teeth. We suggest that here again, interfacial free energy terms strongly influence the reaction kinetics and equilibria.

INTERFACIAL FREE ENERGY, SOLUBILITY AND PARTICLE SIZE

It has been recognized for several decades that there is a close relationship between solubility, S_∞, and

interfacial tension (γ_{SL}) between a solid (S) and a liquid (L). The earliest treatment of this connection was given by Ostwald (ref. 1), subsequently corrected by Freundlich (ref. 2), as Eq. (1)

$$\rho \, v \frac{RT}{M} \ln \frac{S_r}{S_\infty} = \frac{2\gamma_{SL}}{r} \qquad (1)$$

In Eq. (1), S_r is the solubility of particles of size (radius) r, S_∞ is the normal solubility value (of a plane surface), M the molar mass, R the gas constant, T the temperature, and v represents the number of moles of ions formed from one mole of electrolyte. Recently, several similar relationships have been proposed (refs. 3-6) that can be summarized as Eq. (2)

$$\gamma_{SL} = -A_i \ln S_\infty + B_i \qquad (2)$$

where A_i and B_i are constants. Despite the fact that a considerable amount of work has been done to verify Eqs. (1) and (2), there is little unambiguous experimental evidence confirming their validity.

It must be emphasized than an important thermodynamic property in a binary system is ΔG_{SWS}, the free energy change per unit area for the process in which solute surfaces, S, are initially brought into contact with the water, W, with water molecules separating two surfaces of phase S. The free energy change, ΔG_{SWS}, is given by Eq. (3)

$$\Delta G_{SWS} = -2\gamma_{SW} \qquad (3)$$

If ΔG_{SWS} is positive, then the solute surfaces S will repel each other in water, and substance S will spontaneously disperse or dissolve in water. If ΔG_{SWS} is negative, solute surfaces at equilibrium in solution will experience an attraction for each other, and so will tend to precipitate. If ΔG_{SWS} is lies between zero and -1.5 kT, the mean thermal energy per kinetic unit in the system will cause the solutes that have met in a dilute solution to separate again. Hence, $\Delta G_{SWS} > -1.5$ kT represent a general condition for solubility or dispersibility of the solute. In studies of the solubility of organic substances, the molecules of solute are identical in solid and dissolved states, thus facilitating the calculation of the free energy changes. However, when a sparingly soluble salt is dissolved in aqueous solution, the ions in the solution and in the solid crystal phase are completely different The growth unit may be considered as the minimum size of the solute species needed for the elucidation of the interfacial tension or free energy in the process of dissolution.

Since our interest is in the free energy change accompanying each process, we can also treat the solubility in terms of the energies of cohesion of the separate components together with the excess energy of adhesion of the two components. For example, for dissolution, a unit area of crystal surface must come into contact with the liquid phase, and the change in free energy due to adhesion between solid and liquid can be represented by Eq. (4)

$$\Delta G_{SL}^{adhesion} = \gamma_{SL} - \gamma_S - \gamma_L \qquad (4)$$

where γ_S and γ_L are the surface tensions of solid and liquid, respectively. The unit surface is then detached from the bulk crystal into the solution, and the forces balance involving cohesion and adhesion may be represented by Eq. (5)

$$\Delta G_S^{cohesion} + \Delta G_{SL}^{adhesion} - \Delta G_L^{cohesion} = 2\gamma_S + \gamma_{SL} - 2\gamma_L \qquad (5)$$

It can be seen from Eqs. (4) and (5) that a low interfacial tension ,γ_{SL}, together with a high liquid surface tension, γ_L, will facilitate the dissolution of the crystal in the liquid. Water has an unique property to dissolve ionic crystals.

In order to be able to estimate solubility in an aqueous solution, the interfacial tension between the crystal and the solution can alternatively be obtained using contact angle measurements together with surface tension component theory (ref. 7). This is expressed in Eq. (6)

$$\gamma_{SL} = (\sqrt{\gamma_S^{LW}} - \sqrt{\gamma_L^{LW}})^2 + 2(\sqrt{\gamma_S^+\gamma_S^-} + \sqrt{\gamma_L^+\gamma_L^-} - \sqrt{\gamma_S^+\gamma_L^-} - \sqrt{\gamma_S^-\gamma_L^+}) \qquad (6)$$

where γ^{LW} is the Lifshitz-van der Waals (LW) surface tension component (apolar), γ^+ the electron-acceptor (Lewis acid), and γ^- the electron donor (Lewis base) parameter. Surface tension components of synthetic calcium phosphates, summarized in Table 1, show that the hydrophilicities and hydrophobicities vary widely; for example, dicalcium phosphate dihydrate (DCPD) is hydrophilic and

TABLE I. Surface tension components (γ_S in 10^{-3} J m^{-2}) and interfacial tension (γ_{SL} in 10^{-3} J m^{-2}) between water and synthetic calcium phosphates.

Solid	γ_S^{LW}	γ_S^+	γ_S^-	γ_{SL}^C	n	γ_{SL}^{KG}	γ_{SL}^{KD}	$logS_\infty$
DCPD	26.4	1.6	31.7	-4.2	1.3-2.0	0.4	0.4	-2.22
OCP	21.6	2.2	19.7	4.3	2.2-3.3	7.1	2.9	-6.16
HAP	36.2	0.9	16.0	10.0	2.6-4.7	17.1	9.3	-6.44
FAP	32.4	0.6	9.0	18.5	1.4-2.1	30.0	17.1	-6.67

γ_{SL}^C = interfacial tension from contact angle;

γ_{SL}^{KG} = interfacial tension from growth kinetics;

γ_{SL}^{KD} = interfacial tension from dissolution kinetics.

relatively quite soluble while FAP is very hydrophobic and much less soluble. The hydrated layer of OCP is almost certainly hydrophilic in nature and it is more likely than the apatitic layer to form a low energy interface with an aqueous phase. In TABLE I, it can be seen that for HAP, $\gamma^-=16.0 \times 10^{-3}$ J m^{-2} while for OCP, $\gamma^- = 19.7 \times 10^{-3}$ J m^{-2}.

The data in TABLE I clearly demonstrate a parallelism between interfacial tension and solubility, consistent with the model on which equations (2) and (4) are based, namely that during dissolution, some neighboring ions on the surface are replaced by water molecules to form units that escape into the bulk solution. Higher values of γ_{SL} indicate the greater difficulty in forming such as interface between the particles and the aqueous phase resulting in a greater energy requirement for dissolution of the crystal. A_i in Eq. (2) depends theoretically on properties of the crystal such as the size of a growth unit (ref. 8) and there are different slopes for different crystals when plotting $logS_\infty$ as a function of γ_{SL}. Despite the general increase in solubility, with decreasing solid/liquid interfacial tensions (γ_{SL}), a linear relationship between γ_{SL} and $logS_\infty$ is therefore not necessary.

The use of relationships describing crystal solubility as a function of particle size, for determining the interfacial tension at a solid/liquid interface (ref. 8), may be unjustified. The condition of solubility describes the permanent stable equilibrium between solute and solution, in which the quantity of the two phases may be varied at will without influencing the concentration of either as long as both are present. When experiments are carefully executed, a variation of solubility with particle size is rarely observed for freshly precipitated solids (ref. 9).

INTERFACIAL FREE ENERGY, CRYSTALLIZATION AND DISSOLUTION KINETICS

The mechanisms of crystal growth and dissolution are usually interpreted from the measured constant composition reaction rate as a function of thermodynamic driving forces and the effective order of reaction,

n, is determined by fitting the experimental data to an empirical rate law such as Eq. (7)

$$R = k \, \sigma^n \qquad (7)$$

In Eq. (7), k is the effective rate constant and σ, the relative supersaturation or undersaturation with respect to the growing or dissolving phase. The mechanisms of the reactions are then determined by fitting kinetics rate data to crystal growth models, enabling interfacial tensions to be calculated. The effective order of reactions for the calcium phosphate phases of interest in the present paper are summarized in TABLE I, from which can be seen that interfacial tension values between the solutions and each of the mineral phases calculated from the kinetics of crystallization and dissolution are of the same order of magnitude as those obtained from contact angle measurements. This provides strong justifications for the use of these methods to provide information about the mechanisms of crystallization and dissolution of these calcium phosphate phases. The better agreement with dissolution as compared with growth experimental data for the same mineral surface, may be due to the different interfacial adsorption processes involved in crystal growth and dissolution kinetics.

In crystallization reactions, a much smaller interfacial tension value between aqueous media and a solid phase suggests that the phase would have a greater tendency to be nucleated either on itself or on foreign surfaces. Despite the fact that DCPD is the most soluble among the mineral phases in TABLE I, it forms under many physiological, geochemical and laboratory conditions. Hitherto, explanations for the preferential formation of DCPD in terms of reaction mechanism have been only partially successful. In terms of surface tension data (TABLE I), however, this kinetic phenomenon may readily be explained in terms of the low interfacial tension values. At small thermodynamic driving forces for crystallization or dissolution, the low interfacial tensions increase the tendency to precipitate or dissolve. The same arguments can be made for OCP. However, surfaces with low interfacial tensions also indicate thermodynamic instability, which would increase the tendency to transform to more stable apatitic phases. This probably explains why DCPD and OCP have been so frequently implicated as possible precursors to the formation of apatites, especially in biological mineralization reactions involving tooth, bone, and dental calculus formation.

SOLUBILITY, KINETIC PHASE TRANSFORMATION

The state of a system at equilibrium can be concisely expressed in terms of the phase rule of Gibbs:

$$F = C - P + 2 \qquad (8)$$

where F is the number of degrees of freedoms in a system of C components with P phases. For two components at constant temperature and pressure, there are no degree of freedom (F = 0) and so there is a specific reproducible solubility. It is generally accepted that neither the amount of excess solid nor the size of the particles present will change the position of the equilibrium. Paradoxically, both Eqs (1) and (2) suggest that the solubility can be expressed as a function of particle size or specific surface area. This problem has been addressed by Ibl and Dodge (ref. 10) and Good (ref. 11). The Gibbs-Duhem equation, in the form that has been employed in the posing of the problem, was written for constant temperature and pressure. But a binary, 2-phase system at constant temperature and pressure is invariant, according to the Phase Rule. Thus, although Eq. (9) describes the condition of equilibria

$$\mu_i^\alpha = \mu_i^\beta = \mu_i \qquad (9)$$

it cannot be differentiated with respect to composition, as a binary system, since such a differentiation would mean, physically, that the concentration of a component was being varied. This would be impossible in view of the zero variance of the system.

If we assume that the constraints for the constant-temperature-constant pressure 2-phase system are valid, the number of components must be greater than two. Actually, in the derivations of the Eqs. (1) and (2) for

a solid-liquid system, the mass or chemical potential must not be differentiated. Thus, for these systems, Eqs. (1) and (2) cannot be recommended for quantitative discussions of the relationship between solibility, interfacial tension and particle size.

Whenever possible, equilibrium solubility should be approached from both supersaturation and undersaturation at very low driving forces, since one of the problems in determining solubility is the possibility of phase transformation. For the calcium phosphates, DCPD and OCP are the phases that precipitate most readily provided the degree of supersaturation with respect to HAP is sufficiently high so that supersaturation with respect to their phases has also been achieved. Subsequently, these salts tend to convert to thermodynamically more stable forms, sometimes going through a sequence of nonstoichiometic phases of increasing stability, but this can be a slow process. Under circumstances where one of these other salts has formed, it may not be possible to describe the composition of the solution from solubility considerations unless the presence of that salt is also taken into account. This is true even though the salt is metastable with respect to HAP and one or more of the other calcium phosphates. In the light of these problems, caution must be exercised in the interpretation of the measured rates of dissolution and precipitation.

In the free drift and pH-stat experiments, the stoichiometry of the precipitated phase must be determined from small relative changes in the total calcium and phosphate concentrations in the solutions. In order to avoid any change in the nature of the precipitating phase at different driving forces, the difference in the total calcium and phosphate must also be minimized. Thus, small analytical errors in concentrations may cause large uncertainties in the ratio of calcium to phosphate of the precipitate, making phase identification difficult. Using the constant composition method, however, the reaction solution can be maintained at a constant driving force for long periods so that relatively large amounts of new solid phase can be grown. In the studies of transformation of DCPD to OCP, experiments were conducted in solutions undersaturated with respect to DCPD but supersaturated to OCP (ref. 12). It was found that OCP nucleation and growth took place at DCPD surfaces about 30 minutes after their introduction. The constant composition method offers the most senstive technique for monitoring these reactions and their approach to equilibrium.

EXPERIMENTAL

Kinetics of Crystallization

In a typical constant composition crystal growth experiment, a metastable supersaturated solution was prepared in stirred, double-walled Pyrex glass vessels maintained at constant temperature. For calcium phosphates, an atmosphere of presaturated nitrogen gas was maintained in order to exclude carbon dioxide. Background electrolyte such as sodium chloride or potassium nitrate solution was used to maintain the ionic strength. The solution pH was brought to the desired value by the careful slow addition of dilute base (usually, potassium hydroxide). A pH electrode coupled with a single junction reference electrode along with an Orion pH meter was used to monitor changes in hydrogen ion activities. Once equilibrium was attained, the solid phase seeding surfaces were introduced to initiate the crystallization. Any changes in the hydrogen ion activities sensed by electrodes triggered the addition of titrants from stepper motor-driven burets. The volume of titrant, V, added as a function of time was recorded. The induction time, τ_{in}, taken as the time needed to reach steady-state nucleation and growth at the solid surfaces, was measured as the time from addition of seeding surfaces to the intersection of a tangent (dV/dt) with the time axis.

Contact angle measurements

Contact angle measurements were made using a Gaertner (Chicago, IL) telemicroscope with an eyepiece goniometer and Teflon/glass syringes equipped with stainless-steel Luer-tipped hypodermic needles (Gilmont Instruments, Chicago, IL). The advancing contact angles (θ) were directly measured with a drop of the liquids, placed on smooth flat surfaces.

For the determination of the contact angle formed between a liquid (and air, or vapor) and finely divided powder particles, for which direct contact angle measurements cannot be performed, a thin layer wicking capillary rise procedure was used. In this method, the measured rate of capillary rise (i.e. the capillary rise h, in a time t) of a liquid L, through a packed column of powder supported on a glass microscope slide, was substituted into the Washburn Eq. (10) (ref. 7):

$$h^2 = \frac{tR_{eff}\gamma_L \cos\theta}{2\eta} \tag{10}$$

In Eq. (10), R_{eff} is the effective interstitial pore radius, η the viscosity of the liquid, θ the contact angle between the solid (S) and the liquid (L), and γ_L the liquid surface tension against its vapor.

The surface tension component and parameters of the solid particles were calculated by means of Young's equation (11) (ref. 7):

$$(1+\cos\theta)\gamma_L = 2(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^+\gamma_L^-} + \sqrt{\gamma_S^-\gamma_L^+}) \tag{11}$$

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REFERENCES:

1.   W. Ostwald Z. Phys. Chem. **34**, 495 (1900).
2.   H. Freundlich, Colloid & Capillary Chemistry, (E. P. Dutton and Company, Inc.   New York, 1923, p. 153).
3.   A. E. Nielsen and O. Sihnel, J. Crystal Growth, **11**, 233 (1971).
4.   O. Sihnel, J. Crystal Growth, **57**, 101 (1982).
5.   P. Bennema and O. Sihnel, J. Crystal Growth, **102**, 547 (1990).
6.   A. Mersmann, J. Crystal Growth, **102**, 841 (1990).
7.   C. J. van Oss, Interfacial Forces in Aqueous Media, (Marcel Dekker, New York,   1994).
8.   W. Wu and G. H. Nancollas, Adv. Colloid Interface Sci., (in press).
9.   R. D. Vold and M. J. Vold, "Solubility" in Techniques of Organic Chemistry, ed.   A. Weissberger, Vol. 1, p. 297, Interscience Publisher, New York (1949).
10.   N. V. Ible and B. F. Dodge, Chem. Eng. Sci., **2**, 120 (1953).
11.   R. J. Good, Chem. Eng. Education, **21**, 94 (1987).
12.   J. Zhang and G. H. Nancollas, J. Colloid Interface Sci., **152**, 132 (1992).