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Note

SOLUBILITY AND THERMODYNAMIC DATA OF MAGNESIUM HYDROGEN PHOSPHATE IN AQUEOUS MEDIA

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Studies on the solubility of magnesium hydrogen phosphate ($MgHPO_4 \cdot H_2O$) are considered relevant in explaining the role of Mg^{2+} in the inhibition [1,2] of dicalcium phosphate, $CaHPO_4 \cdot 2\,H_2O$ (DCPD) and octacalcium phosphate, $Ca_8H_2(PO_4)_6 \cdot 5\,H_2O$ (OCP), the precursors in the formation of crystalline calcium hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ (HAP), the model inorganic component of human skeletal system [3]. The solubility product (K_{sp}) and related thermodynamic parameters, ΔG^0, ΔH^0, ΔS^0 and ΔC_p^0 of $MgHPO_4 \cdot H_2O$ in aqueous media at pH 7.2 under a constant ionic environment of 0.165 M $NaNO_3$ between temperatures of 30 and 50°C have been calculated and reported.

EXPERIMENTAL

$MgHPO_4 \cdot H_2O$ was precipitated at room temperature (30°C) by the dropwise addition of a 20% solution of $MgSO_4 \cdot 7\,H_2O$ to a 9% solution of $Na_3(PO_4) \cdot 12\,H_2O$ as required for stoichiometric precipitation for a yield of 5.0 g. Mixing of the reagents was completed within about 1.5 h. The precipitate was filtered, washed repeatedly with water, alcohol and ether. The sample was dried in vacuo for 24 h before subjecting it to chemical analysis. Percentage loss of weight of the sample on heating at 100°C at 6 h showed that the sample was a monohydrate. The experimental weight percents [4] of Mg = 17.30 and P = 23.10 were found to be close to the theoretical values of Mg = 17.40 and P = 22.90. Solubility of the sample was determined at 30, 37.5, 40, and 50°C and pH 7.2 maintained by a borax–boric acid buffer by the method of equilibration used earlier [5].

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RESULTS AND DISCUSSION

Calculation of solubility product and thermodynamic data

The solubility product (K_{sp}) of the sample was calculated from the experimentally determined magnesium, phosphorus and the final pH of the medium. The changes in pH before and after equilibration were within ±0.1. The total phosphorus content (P_T) in the filtrate was divided into HPO_4^{2-} and PO_4^{3-} species by using the following relationships

$$P_T = C_{PO_4^{3}} \left[\frac{(H^+)^3}{K_1 K_2 K_3} + \frac{(H^+)^2}{K_2 K_3} + \frac{(H^+)}{K_3} + 1 \right] \tag{1}$$

$$K_3 = \frac{C_{PO_4^{3}} \times (H^+)}{[HPO_4^{2-}]} \tag{2}$$

assuming unitary values for the respective activity coefficients and K_1, K_2, K_3 being the dissociation constants of orthophosphoric acid. The presence of $H_2PO_4^-$ was not considered since the existence of this species is negligible at the pH under investigation. The ionic strength of the medium was then calculated by using the equation

$$\mu = \tfrac{1}{2} \sum C_i Z_i^2 \tag{3}$$

where the terms have their usual significance. Activity coefficients were calculated by using the Davis equation

$$\log f_{(\text{ion})} = A_{\text{ion}} Z_{\text{ion}}^2 \sqrt{\mu} \tag{4}$$

where A is the standard temperature dependent constant, the value of μ was refined by the method of iteration until a constant value of μ was obtained.

TABLE 1

Activity and activity coefficients of different ionic species present in saturated solutions of $MgHPO_4 \cdot H_2O$ at various temperatures

Temp. (°C)	Total P, g-ions per litre ($\times 10^3$)	Activity			Activity coefficient		
		(Mg^{2+}) $\times 10^3$	(HPO_4^{2-}) $\times 10^3$	(PO_4^{3-}) $\times 10^8$	$f_{Mg^{2+}}$	$f_{HPO_4^{2-}}$	$f_{PO_4^{3}}$
30	4.00	1.3431	0.2509	0.0278	0.1599	0.1599	0.0161
37.5	2.64	0.3898	0.1772	0.0206	0.1695	0.1695	0.0184
40	2.78	0.4989	0.1815	0.0211	0.1663	0.1663	0.0176
50	2.32	0.4743	0.0325	0.4379	0.1581	0.1581	0.0157

The calculated values of activity coefficients for all the species are given in Table 1.

It is clear from the table that the contribution of PO_4^{3-} ions to the process of dissolution is negligible as compared with the concentrations of HPO_4^{2-} in the medium. The solubility product K_{sp} for $MgHPO_4 \cdot H_2O$ was then obtained by the equation

$$K_{sp} = [Mg^{2+}]\, f_{Mg^{2+}} \times (HPO_4^{2-})$$

where (HPO_4^{2-}) is the activity of HPO_4^{2-} ion. The values of K_{sp} at various temperatures were fitted by the method of least squares to an equation

$$-\log K_{sp} = \frac{A_m}{T} + B_m + C_m T \tag{5}$$

The values of the constants A, B and C in eqn. (5) were found to be: 8b-67363.612, 427.978 and -0.65839, respectively. Standard thermodynamic quantities ΔG^0, ΔH^0, ΔS^0 and ΔC_p^0 of the dissolution process have been calculated by using the values of A, B and C from the following equations

$$\Delta G^0 = -2.303\, R(A_m + B_m T + C_m T^2) \tag{6}$$

$$\Delta H^0 = 2.303\, R(A_m - C_m T^2) \tag{7}$$

$$\Delta S^0 = -2.303\, R(B + 2\, C_m T) \tag{8}$$

$$\Delta C_p^0 = -2.303\, R(2\, C_m T) \tag{9}$$

where R is the gas constant. For $MgHPO_4 \cdot H_2O$, $m = 1$, since the function refers to the simple dissolution of $MgHPO_4$ as follows

$$MgHPO_{4(s)} \rightleftharpoons Mg^{2+}_{(aq)} + HPO^{2-}_{4(aq)} \tag{10}$$

The results of the standard thermodynamic parameters and the values of pK_{sp} at different temperatures are given in Table 2. It is observed that both the values of ΔG^0 and the negative value of ΔH^0 increased and the negative value of ΔS^0 decreased with increase of temperature. These observations lend support to the view that $MgHPO_4 \cdot H_2O$ exhibits retrograde solubility behaviour.

Since the values of $pK_{sp}(-\log K_{sp})$ of $MgHPO_4 \cdot H_2O$ given in Table 2 are of comparable order and magnitude to those of DCPD [6,7], precipitation of the former, during hydrolysis of DCPD or OCP in the presence of Mg^{2+} in aqueous media cannot be ruled out. The reported inhibitory effect of Mg^{2+} on hydrolysis of DCPD or OCP, the possible precursors for HAP, may be due to association of the additional phase of $MgHPO_4 \cdot H_2O$ formed during hydrolysis.

TABLE 2

Thermodynamic parameters of the dissolution of $MgHPO_4 \cdot H_2O$ at pH 7.2 and temperatures between 30 and 50°C

Temp. (°C)	pK_{sp} values		$\Delta G^0 \times 10^{-4}$ (J $mole^{-1}$ deg^{-1})	$(-)\Delta H^0 \times 10^{-6}$ (J $mole^{-1}$)	$(-)\Delta S^0 \times 10^{-2}$ (J $mole^{-1}$ deg^{-1})	$\Delta C_p^0 \times 10^{-3}$ (J $mole^{-1}$ deg^{-1})
	Exptl.	Calc.				
30	6.3718	6.1620	3.5743	2.4467	5.5498	7.6381
37.5	6.7815	6.5734	3.9010	2.5008	3.7852	7.8146
40	6.7515	6.0810	4.0032	2.5244	3.0289	7.8902
50	6.8283	6.7602	4.1801	2.6045	0.5081	8.1045

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