Thermochimica Acta, 70 (1983) 163–171
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SOLUBILITY AND THERMODYNAMIC DATA OF MANGANESE HYDROGEN PHOSPHATE IN THE SYSTEM $MnO-P_2O_5-H_2O$ AT 35, 40, 45 AND 50°C

P.P. MAHAPATRA *, A.K. DASH and N.S. CHICKERUR

Post-Graduate Department of Chemistry, Khallikote College, Berhampur (Gm) 760001 (India)

(Received 12 May 1983)

ABSTRACT

Manganese hydrogen phosphate monohydrate, $MnHPO_4 \cdot H_2O$, a new phase, is synthesized. Its solubility is investigated in the temperature range 35–50°C and pH range 3.4–7.5. K_{sp}, ΔH^0, ΔS^0 and ΔG^0 for the dissolution are reported. The decrease in solubility with increase in pH is explained as due to a surface coating of insoluble basic phosphate.

INTRODUCTION

Although $MnHPO_4 \cdot 3\ H_2O$ was known earlier [1], manganese hydrogen phosphate monohydrate, $MnHPO_4 \cdot H_2O$ (hereafter DMPM), is now found to be another important stable phase in the $MnO-P_2O_5-H_2O$ system. This phase has been characterized and its solubility behaviour studied to determine its stability range. Thermodynamic properties have also been investigated in order to understand the interrelations with the calcium phosphates that precipitate from aqueous solutions since manganese is considered to participate in some way in promoting classification of bones in vivo [2,3].

The present work reports the solubility of DMPM, K_{sp}, standard heat, entropy, and enthalpy of the dissolution reaction at 35, 40, 45 and 50°C between pH 3.4 and 7.5.

EXPERIMENTAL

$MnHPO_4 \cdot H_2O$ is prepared by adding phosphoric acid to a known weight of manganese sulphate according to the equation

$$MnSO_4 + H_3PO_4 + 2\ NaOH \xrightarrow{pH\ 6.0} MnHPO_4 \cdot H_2O + Na_2SO_4 + H_2O \qquad (1)$$

---

* To whom correspondence should be addressed.

The pH of the mixed solution was brought to 6.0 by the drop-wise addition of 0.05 M sodium hydroxide solution. The precipitate was filtered, washed with double-distilled water, alcohol, and ether, air-dried, and analyzed complexometrically [4]. The IR spectra of the sample were obtained on KBr pellets. Thermal dehydration of the sample was studied by heating 100 mg of the substance of 200 mesh up to 400°C.

Equilibration was done by the method used earlier [5] between 35 and 50°C at pH 3.4–7.5 under a constant ionic environment of 0.05 M $NaNO_3$. The experiments were performed in order to determine the solubility isotherm and solubility product of DMPM. Equilibration of DMPM in dilute phosphoric acid was used for this purpose.

RESULTS AND DISCUSSION

The analytical results (found (%): Mn 32.02, P 18.54, and Mn : P g atom ratio 0.99; Calcd (%): Mn 32.82, P 18.33, and Mn : P g atom ratio 1.0) correspond to $MnHPO_4 \cdot H_2O$. The IR spectra showed absorption maxima at 3380, 3339, 2352, 1640, 1128, 1065, 995, 981, 865 and 665 cm^{-1} corresponding to hydrated dicalcium phosphate [6]. The percent weight loss on thermal dehydration of the sample was found to be maximum at 180°C, corresponding to the loss of one molecule of water. After thermal treatment, analysis of the sample gave Mn 36.52%, P 19.49% (Mn : P g atom ratio 1.05), indicating that the sample is anhydrous $MnHPO_4$.

CALCULATION OF SOLUBILITY PRODUCT AND STANDARD THERMODYNAMIC PARAMETERS

The ionic strength, μ, is defined as

$$\mu = P\left[Q + \frac{H^+}{2P} + \theta + \phi\right] + X_i \tag{2}$$

Where P and H^+ represent the molar concentrations of phosphorus and hydrogen ion, respectively. The other terms in eqn. (2) are

$$Q = \frac{2\,M}{P} \tag{3}$$

$$\theta = \frac{(H^+)}{2\,K_2 f_{H_2PO_4^-}} + \frac{2}{f_{HPO_4^{2-}}} \tag{4}$$

$$\phi = \frac{(H^+)^2}{K_1 K_2} + \frac{(H^+)}{K_2 f_{H_2PO_4^-}} + \frac{1}{f_{HPO_4^{2-}}} \tag{5}$$

X_i in eqn. (2) refers to the molar concentrations of the other ionic species of the equilibration medium. In eqns. (3)–(5) (H^+) and M represent the hydrogen ion activity and molar concentrations of manganese(II) ion, respectively. K_1 and K_2 are the first and second dissociation constants for H_3PO_4, and $f_{H_2PO_4^-}$ and $f_{HPO_4^{2-}}$ are the molar activity coefficients for the species $H_2PO_4^-$ and HPO_4^{2-}. In eqns. (4,5) it is considered that the only ionic species present in significant concentrations are HPO_4^{2-} and $H_2PO_4^-$. Assuming the unitary values of $f_{H_2PO_4^-}$ and $f_{HPO_4^{2-}}$, an approximate ionic strength was obtained. An improved ionic activity coefficient, f_i, was then calculated from the Debye–Hückel limiting law

$$-\log f_i = \frac{Az_i\sqrt{\mu}}{1 + Ba_i\sqrt{\mu}} \tag{6}$$

The values $a_i = 6 \times 10^{-8}$ for Mn^{2+} and $a_i = 4 \times 10^{-8}$ and 4.5×10^{-8} for HPO_4^{2-} and $H_2PO_4^-$, respectively, were used. By the process of iteration, a constant μ was obtained and activity coefficient f_i determined. Using $\log f_i$ in eqn. (5), the activity of HPO_4^{2-} (HPO_4^{2-}) was calculated from $(HPO_4^{2-}) = P/\phi$. The solubility product, K_{sp} of DMPM was then obtained using

$$K_{sp} = M f_{Mn} \times \left(HPO_4^{2-}\right) \tag{7}$$

K_{sp} at various temperatures and pH values are calculated by

$$\mathrm{P}\,K_{sp} = \frac{A_m}{T} + B_m + C_m T \tag{8}$$

The equations with the numerical values of A, B and C used for the calculations for pH 3.4–7.5, respectively, are

$$\mathrm{P}\,K_{sp} = -\frac{1811.155}{T} + 15.233 - 0.0063\,T \tag{9}$$

$$\mathrm{P}\,K_{sp} = -\frac{17302.209}{T} + 122.204 - 0.1578\,T \tag{10}$$

$$\mathrm{P}\,K_{sp} = -\frac{798.633}{T} + 0.6085 + 0.0138\,T \tag{11}$$

$$\mathrm{P}\,K_{sp} = -\frac{16556.618}{T} + 108.901 - 0.1548\,T \tag{12}$$

$$\mathrm{P}\,K_{sp} = -\frac{26363.596}{T} + 172.641 - 0.2585\,T \tag{13}$$

The values of the thermodynamic parameters were obtained from eqns. (14)–(17).

$$\Delta G^0 = -RT \ln K_m = -R\left(A_m + B_m T + C_m T^2\right) \tag{14}$$

$$\Delta S^0 = -\left(\partial \Delta G^0 / \partial T\right) = -R\left(B_m + 2\,C_m T\right) \tag{15}$$

$$\Delta H^0 = \Delta G^0 + T\Delta S^0 = R\left(A_m + 2\,C_m T\right) \tag{16}$$

$$\Delta C_p{}^0 = \left(\partial \Delta H^0 / \partial T\right) = -R\left(2\,C_m T\right) \tag{17}$$

TABLE 1

Solubility of manganese hydrogen phosphate monohydrate at 35°C

Initial phosphorus $P_0 \times 10^4$ (g/50 ml)	pH	Composition of the equilibrium solutions (g atom l^{-1})		Mn/P_f	$K_{sp} \times 10^8$
		$P_f \times 10^4$	$Mn \times 10^4$		
6.740	3.4	25.6	3.49	0.136	3.6386
3.370	4.5	15.2	2.79	0.1835	3.7892
0.8425	5.8	12.35	3.05	0.2469	3.2575
0.42125	6.5	21.3	1.64	0.0769	3.3056
0.1685	7.5	11.3	2.79	0.2469	3.1693

Average $K_{sp} = 3.43204$.
Standard deviation = 0.2578.

TABLE 2

Solubility of manganese hydrogen phosphate monohydrate at 40°C

Initial phosphorus $P_0 \times 10^4$ (g/50 ml)	pH	Composition of the equilibrium solutions (g atom l^{-1})		Mn/P_f	$K_{sp} \times 10^8$
		$P_f \times 10^4$	$Mn \times 10^4$		
6.740	3.4	15.6045	5.79	0.3710	3.1760
3.370	4.5	5.19	5.39	1.0385	3.0578
0.8425	5.8	4.99	5.199	1.0418	3.0487
0.42125	6.5	5.48	4.69	0.8558	2.8139
0.1685	7.5	5.55	5.389	0.9709	2.8711

Average $K_{sp} = 2.99332$.
Standard deviation = 0.1480.

TABLE 3

Solubility of manganese hydrogen phosphate monohydrate at 45°C

Initial phosphorus $P_0 \times 10^4$ (g/50 ml)	pH	Composition of the equilibrium solutions (g atom l^{-1})		Mn/P_f	$K_{sp} \times 10^8$
		$P_f \times 10^4$	$Mn \times 10^4$		
6.740	3.4	8.75	5.99	0.6845	3.2676
3.370	4.5	6.75	5.68	0.8414	2.5340
0.8425	5.8	6.328	5.499	0.8689	2.9125
0.42125	6.5	6.349	5.290	0.8332	2.9201
0.1685	7.5	6.477	5.019	0.7748	2.9930

Average $K_{sp} = 2.02544$.
Standard deviation = 0.2039.

TABLE 4

Solubility of manganese hydrogen phosphate monohydrate at 50°C

Initial phosphorus $P_0 \times 10^4$ (g/50 ml)	pH	Composition of the equilibrium solution (g atom l^{-1})		Mn/P_f	$K_{sp} \times 10^8$
		$P_f \times 10^4$	$Mn \times 10^4$		
6.740	3.4	6.53	5.25	0.8039	2.8626
3.370	4.5	4.11	5.99	1.4574	2.2151
0.8425	5.8	5.25	5.57	1.0609	2.7163
0.42125	6.5	4.86	4.58	0.9423	2.1306
0.1685	7.5	12.16	2.59	0.2129	3.0055

Average $K_{sp} = 2.59602$.
Standard deviation = 0.41766.
$P_f = (P - P_0)$, where P is the total phosphorous concentration of the equilibrating medium.

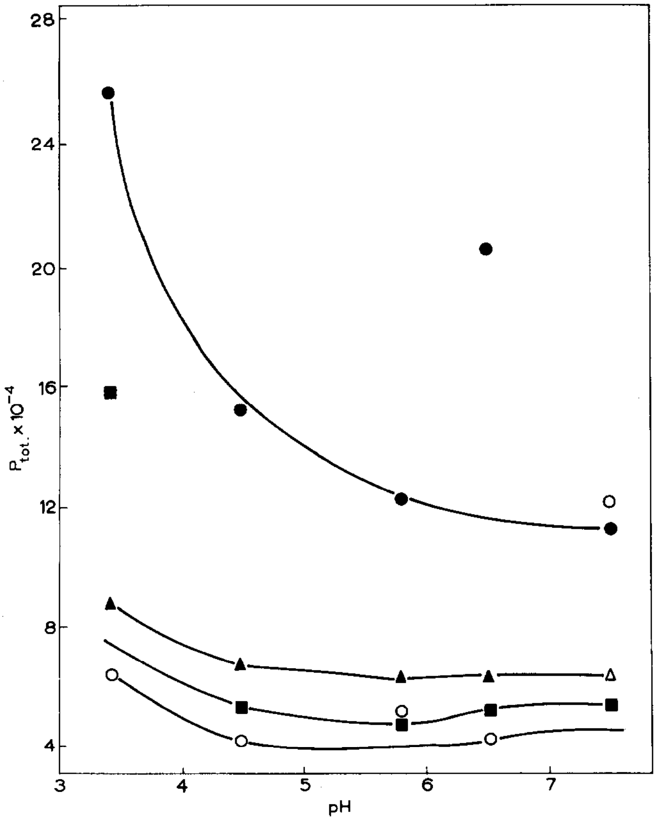

Fig. 1. Solubility isotherm of manganese hydrogen phosphate monohydrate between pH 3.4 and 7.5 at ●, 35°C; ■, 40°C; ▲, 45°C; ⊙, 50°C.

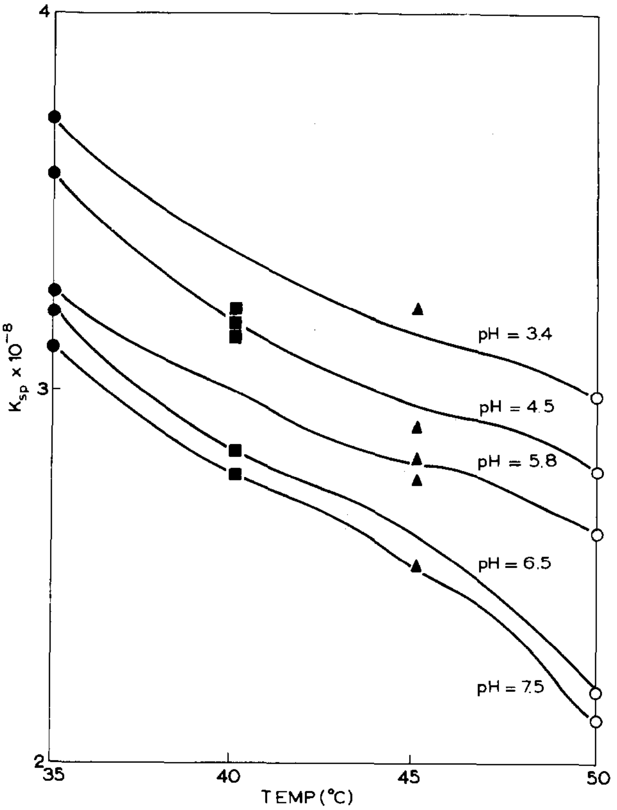

Fig. 2. Dependence of solubility product (K_{sp}) of manganese hydrogen phosphate monohydrate on pH and temperature of investigation. ●, 35°C; ■, 40°C; ▲, 45°C; ⊙, 50°C.

Where R is the gas constant. For DMPM ($m = 1$) the function refers to the dissolution of one mole of $MnHPO_4 \cdot H_2O$ according to the reaction

$$MnHPO_4 \cdot H_2O = Mn^{2+} + HPO_4^{2-} + H_2O \tag{18}$$

The composition of the saturated solutions of DMPM at four temperatures are summarized in Tables 1–4. Congruent dissolution of the salt is observed from the values of Ca: $(P - P_0)$ ratio at temperatures 40–50°C, while at 35°C the value departed from unity. The solubility product (K_{sp}) which decreased with increase in temperature is given in the last columns. Variations in the solubility of the sample with increase in hydroxyl ion concentration of the medium is probably due to a coating of a very thin layer of an insoluble basic phosphate over the surface of the sample. This consequently resulted in a decrease in solubility of DMPM with increase in pH, indicated by the MN : P g atom ratio of 1.20 to 1.25 of the solid obtained between pH 6.5 and 7.5 and 0.83 to 1.05 in the pH range 3.4–5.8.

Figures 1 and 2 show the solubility isotherm for DMPM in terms of total

TABLE 5

Comparison of experimental and calculated values of $-\log K_{sp}$ of manganese hydrogen phosphate monohydrate at different pH and temperatures

$-\log K_{sp}$	35°C	40°C	45°C	50°C
pH = 3.4				
Exptl.	7.4390	7.4981	7.4857	7.5432
Theoret.	7.5857	7.5276	7.4649	7.3993
pH = 4.5				
Exptl.	7.4214	7.5145	7.5965	7.6545
Theoret.	7.4171	7.5253	7.6053	7.5535
pH = 5.8				
Exptl.	7.439	7.498	7.485	7.543
Theoret.	7.399	7.462	7.521	7.543
pH = 6.5				
Exptl.	7.4807	7.5506	7.5346	7.6714
Theoret.	7.4581	7.5427	7.6002	7.6321
pH = 7.5				
Exptl.	7.4910	7.5419	7.5238	7.5220
Theoret.	7.4000	7.4745	7.5058	7.4963

TABLE 6

Thermodynamic parameters for the dissolution of manganese hydrogen phosphate monohydrate at pH 3.4 between 35 and 50°C

Temp. (°C)	ΔG^0 (kcal mole^{-1})	ΔH^0 (kcal mole^{-1})	$\Delta S^0 \times 10^3$ (kcal mole^{-1})	$\Delta C_p^0 \times 10^3$ (kcal mole^{-1})
35	43.63195	23.15678	−336.4003	74.7768
40	44.71318	22.77987	−367.6142	75.9907
45	45.78831	22.39688	−368.8281	77.2046
50	46.86494	22.015389	−370.0420	78.4185

TABLE 7

Thermodynamic parameters for the dissolution of manganese hydrogen phosphate monohydrate at pH = 4.5 and between 35 and 50°C

Temp. (°C)	ΔG^0 (kcal mole^{-1})	ΔH^0 (kcal mole^{-1})	$\Delta S^0 \times 10^3$ (kcal mole^{-1})	$\Delta C_p^0 \times 10^3$ (kcal mole^{-1})
35	43.740155	−44.6005	−286.8036	1861.223
40	45.0958	−35.2160	−256.5874	1891.439
45	46.3032	−25.6833	−226.3727	1921.654
50	47.3595	−15.9995	−210.7896	1937.237

TABLE 8

Thermodynamic parameters for the dissolution of manganese hydrogen phosphate monohydrate at pH = 5.8 and between 35 and 50°C

Temp. (°C)	ΔG^0 (kcal mole^{-1})	$\Delta H^0 \times 10^3$ (kcal mole^{-1})	$\Delta S^0 \times 10^3$ (kcal mole^{-1})	$\Delta C_p^0 \times 10^3$ (kcal mole^{-1})
35	44.1109	−9945.2509	−175.507	−163.3327
40	44.9951	−10771.192	−178.158	−166.5780
45	45.8829	−11600.753	−180.8271	−169.1781
50	46.8033	−12462.997	−183.4871	−171.8381

TABLE 9

Thermodynamic parameters for the dissolution of manganese hydrogen phosphate monohydrate at pH 6.5 and between 35 and 50°C

Temp. (°C)	ΔG^0 (kcal mole^{-1})	ΔH^0 (kcal mole^{-1})	$\Delta S^0 \times 10^3$ (kcal mole^{-1})	$\Delta C_p^0 \times 10^3$ (kcal mole^{-1})
35	43.99233	−35.764612	−268.95113	1825.8468
40	45.21491	−26.56128	−229.3107	1855.4872
45	46.28544	−17.20973	−199.6703	1885.1276
50	47.20970	−7.70999	−170.0030	1914.7680

TABLE 10

Thermodynamic parameters for the dissolution of manganese hydrogen phosphate monohydrate at pH 7.5 and between 35 and 50°C

Temp. (°C)	ΔG^0 (kcal mole^{-1})	ΔH^0 (kcal mole^{-1})	$\Delta S^0 \times 10^3$ (kcal mole^{-1})	$\Delta C_p^0 \times 10^3$ (kcal mole^{-1})
35	43.63251	−35.08514	−225.5768	−3049.4461
40	44.78663	−19.71415	−206.0728	−3098.9501
45	45.69238	−4.09564	−156.5688	−3148.4541
50	46.3523	+11.770384	−107.0648	−3197.3581

concentration of phosphorus over the pH range of investigation at four different temperatures and the dependence of K_{sp} over the temperature range of investigation, respectively. The relative portion of the isotherm in Fig. 1 and the nature of the curve in Fig. 2 show that the solubility of DMPM decreases with increase in temperature. Similarly, smooth curves are also obtained if the concentration of manganese is plotted against pH.

The calculated and experimental values of P K_{sp} ($= -\log K_{sp}$) are compared in Table 5. The results of standard thermodynamic parameters at different pH values and temperatures are given in Tables 6–10. In general the negative value of ΔH^0 at a given pH and temperature indicated an exothermic process of dissolution. The values of standard free energy, heat, and entropy terms at a fixed pH with rise of temperature lend support to the rectrograde solubility behaviour of DMPM.

ACKNOWLEDGEMENT

The authors thank the University Grants Commission, India, for financial support for this investigation.

REFERENCES

1 J.E. Salmon and H. Terry, J. Chem. Soc., (1950) 2813.
2 E. Jal and K. Guggenhein, J. Biochem., 95 (1965) 94.
3 E. Jal and K. Guggenhein, Nat. Dicta, 7 (1965) 62.
4 P.P. Mahapatra, A.K. Dash and N.S. Chickerur, Curr. Sci., submitted for publication.
5 P.P. Mahapatra, H. Mishra and N.S. Chickerur, Thermochim. Acta, 52 (1982) 333.
6 B.O. Fowler, E.C. Moreno and W.E. Brown, Arch. Oral Biol., 2 (1966) 447.