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Solid–liquid phase equilibria of ($Mg(H_2PO_2)_2 + H_2O$), ($Mg(H_2PO_2)_2 + NaH_2PO_2 + H_2O$) and ($Mg(H_2PO_2)_2 + MgCl_2 + H_2O$) systems

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A B S T R A C T

Magnesium hypophosphite $Mg(H_2PO_2)_2$ is an important hypophosphite, and used as an drugs for the treatment of rheumatoid arthritis, plastic stabilizer, flameresistant material, fertilizer additive and the amendment of the soil, which can be synthesized via neutralization reaction and double decomposition reactions. In this work, the (solid + liquid) phase diagrams of ($Mg(H_2PO_2)_2 + H_2O$) binary systems, and ($Mg(H_2PO_2)_2 + NaH_2PO_2 + H_2O$), ($Mg(H_2PO_2)_2 + MgCl_2 + H_2O$) ternary systems at 298.15 K were experimentally determined via the classical isothermal solubility equilibrium method. It was found that (1) two solid salts of $Mg(H_2PO_2)_2 \cdot 6H_2O$ and $Mg(H_2PO_2)_2$ with transition temperature 325.15 K occur in the ($Mg(H_2PO_2)_2 + H_2O$) binary system, (2) three solid salts of $Mg(H_2PO_2)_2 \cdot 6H_2O$, $NaH_2PO_2 \cdot H_2O$ and one incompatible double salt [$NaMg(H_2PO_2)_3$] exist in ($Mg(H_2PO_2)_2 + NaH_2PO_2 + H_2O$) system, (3) $Mg(H_2PO_2)_2 \cdot 6H_2O$, $MgCl_2 \cdot 6H_2O$ and one unknown double salt exist in ($Mg(H_2PO_2)_2 + MgCl_2 + H_2O$) system, the unknown double was identified to be an incompatible double salt [$Mg_2(H_2PO_2)_2Cl_2 \cdot 6H_2O$].

1. Introduction

Magnesium hypophosphite $Mg(H_2PO_2)_2$ is an important hypophosphite, and used as an drugs for the treatment of rheumatoid arthritis, plastic stabilizer, flame-resistant material, fertilizer additive and the amendment of the soil [1]. Studies have also shown that it can be used for treating obesityin humans [2].

Magnesium hypophosphite can be synthesized via neutralization reaction of hypophosphorous acid (H_3PO_2) and magnesium hydroxide $Mg(OH)_2$, or double decomposition reactions of sodium hypophosphite (NaH_2PO_2) and soluble magnesium salts, such as magnesium chloride, nitrate, sulfuric [1]. Double decomposition reactions are commonly adopted because of their advantages, such as (1) no venomous gas (PH_3 or H_3PO_3) occurring in the processes and (2) easily controlled production of $Mg(H_2PO_2)_2$ with a distinct crystalline morphology, particle size and purity.

(Solid + liquid) phase equilibria (SLE) data and phase diagrams are essential for process development, design and control [3]. Some SLE of $H_2PO_2^-$-containing systems have been studied, for example, in the hydrometallurgy process of manganese, barium and zinc, the relative systems.

R.M. Dolinina: Na^+,Mn^{2+},NH_4^+ and $H_2PO_2^-$ contained ternary aqueous systems at 293.15 K [4].

Aliev: Na^+-Mn^{2+}//Cl^--$(H_2PO_2)^-$-H_2O quaternary systems at 293.15 K [5].

Alisoglu: Na^+-Mn^{2+}//NO_3^--$(H_2PO_2)^-$-H_2O at 273.15 K [6].

Alisoglu: Na^+-Mn^{2+}//Cl^--$(H_2PO_2)^-$-H_2O at 298.15 K [7].

Alisoglu: K^+-Mn^{2+}//Br^--$(H_2PO_2)^-$-H_2O at 298.15 K [8].

Alisoglu: Na^+-Mn^{2+}//Br^--$(H_2PO_2)^-$-H_2O at 278.15 K [9].

H. Erge: Na^+-Ba^{2+}//Cl^--$(H_2PO_2)^-$-H_2O at 273.15 K [10].

V. Adiguzel: Na^+-Zn^{2+}//Cl^--$(H_2PO_2)^-$-H_2O at 273.15 K [11].

In the fine chemicals process, H. Zhou group concern on production of $Ca(H_2PO_2)_2$, $Al(H_2PO_2)_3$, $Mg(H_2PO_2)_2$ etc. the SLE data of (Ca^{2+}+ Na^+)//(Cl^- + $(H_2PO_2)^-$ + H_2O) at 298.15 K [12] and 323.15 [13] have been reported.

However, SLE data for (Mg^{2+} + Na^+)//(Cl^--$(H_2PO_2)^-$-H_2O) system and subsystems are not found in the opening literatures unless the subsystem of ($NaCl$–$MgCl_2$–H_2O) [14]. In this study, we focus on the (solid + liquid) equilibria of $Mg(H_2PO_2)_2$ contained binary system of ($Mg(H_2PO_2)_2$ + H_2O), ternary systems of ($Mg(H_2PO_2)_2 + NaH_2PO_2 + H_2O$) and ($Mg(H_2PO_2)_2 + MgCl_2 + H_2O$)

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Table 1
Provenance and mass fraction purity of the chemicals used in this study.

Chemical	CAS no.	Source	Initial mass fraction purity	Analysis method
Magnesium chloride hexahydrate	7791-18-6	A.R.[a]	0.990[b]	EDTA method for Mg^{2+} and $AgNO_3$ method for Cl^-
Magnesium hypophosphite hexahydrate	10377-57-8	Own product	0.990[c]	EDTA method for Mg^{2+} and $Na_2S_2O_3$ method for $H_2PO_2^-$
Sodium hypophosphite monohydrate	10039-56-2	A.R.[a]	0.990[d]	$Na_2S_2O_3$ method for $H_2PO_2^-$

[a] A.R. from Tianjin Guangfu Fine Chemical Research Institute.
[b] Record by $MgCl_2 \cdot 6H_2O$.
[c] Record by $Mg(H_2PO_2)_2 \cdot 6H_2O$.
[d] Record by $NaH_2PO_2 \cdot H_2O$.

and report the results of SLE data and phase diagram.

2. Experimental

2.1. Chemicals and apparatus

2.1.1. Chemicals

The chemicals used in this study are described in Table 1. Double deionized water with conductivity lower than 1×10^{-4} S m^{-1} and pH of 6.60 at 298.15 K was used to prepare the solid–liquid mixtures employed for the experiments and chemical analysis. Magnesium hypophosphite hexahydrate was synthesized in our lab at room temperature, via the reaction of $2NaH_2PO_2 \cdot H_2O + MgCl_2 \cdot 6H_2O \rightarrow Mg(H_2PO_2)_2 \cdot 6H_2O + NaCl + H_2O$, and purified by recrystallization.

2.1.2. Apparatus

The (solid + liquid) phase equilibria measurements of the $(Mg(H_2PO_2)_2 + H_2O)$ binary system and $(Mg(H_2PO_2)_2 + NaH_2PO_2 + H_2O)$, $(Mg(H_2PO_2)_2 + MgCl_2 + H_2O)$ ternary systems were carried out in a double jacketed (an oil and vacuum jacket) equilibrium tank (2000 mL, Chemglass Scientific Apparatus) with a mechanical stirrer (Heidolph). The temperature of the (solid + liquid) mixtures were measured with a PT 100 platinum resistance thermometer and controlled by a thermostatic oil bath (K6s-cc-NR, Huber) and a CC-pilot controller. The temperature of the solid–liquid mixture was stable (±0.05 K).

2.2. Experimental procedure

The isothermal solubility equilibrium methodology was adopted to study SLE. For $Mg(H_2PO_2)_2$ saturated curve of $(Mg(H_2PO_2)_2 + H_2O)$ binary system, the SLE experiments were starts from one initial (solid + liquid) mixture with 300 g magnesium hypophosphite hexahydrate and 100 g water at 298.15 K, the mixture was successively heated up to boiling point in steps, or cooled down to eutectic temperature in steps. At each step, the SLE was achieved by mechanical rabbling for least one day and confirmed by the mass percent change of Mg^{2+} concentration less than 0.02% in liquid phase. For ice curve, the different concentration of $(Mg(H_2PO_2)_2 + H_2O)$ solution were prepared at room temperature and cooled down to the ice point, where the temperature will unchanged with further cooling.

For $(Mg(H_2PO_2)_2 + NaH_2PO_2 + H_2O)$ ternary system, for example, in order to determine $Mg(H_2PO_2)_2$ saturated region, an initial SLE mixture was set up by mixing 200 g water and 120 g Magnesium hypophosphite hexahydrate at 298.15 K. And then, one set of SLE experiments were carried out via adding a given amount of $NaH_2PO_2 \cdot H_2O$ in stages until the invariant point was found.

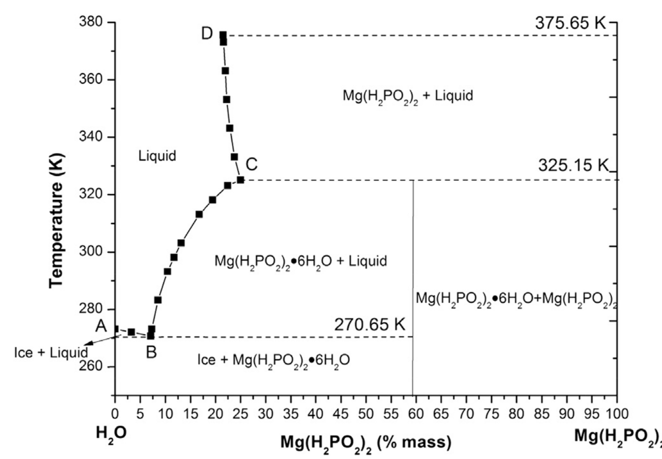

Fig. 1. Phase diagram of $(Mg(H_2PO_2)_2 + H_2O)$ binary system under $p = 101.3$ kPa. A: freezing point of water, B: Eutectic temperature of ice and $Mg(H_2PO_2)_2 \cdot 6H_2O$, C: Alter point of $Mg(H_2PO_2)_2 \cdot 6H_2O$ and $Mg(H_2PO_2)_2$, D: Boiling point of $Mg(H_2PO_2)_2$ saturated solution.

Table 2
(Solid + liquid) equilibria data for the $(Mg(H_2PO_2)_2 + H_2O)$ binary system at $P = 101.3$ kPa.[a]

Temperature K	Liquid phase (%)	Solid	Temperature K	Liquid phase (%)	Solid[b]
	$Mg(H_2PO_2)_2$			$Mg(H_2PO_2)_2$	
273.15	0.00	Ice	318.15	19.45	S_1
272.05	3.23	Ice	323.15	22.43	$S_1 + Mg(H_2PO_2)_2$
270.65	7.09	S_1 + ice	325.15	25.01	$Mg(H_2PO_2)_2$
273.15	7.31	S_1	333.15	23.78	$Mg(H_2PO_2)_2$
283.15	8.52	S_1	343.15	22.86	$Mg(H_2PO_2)_2$
293.15	10.41	S_1	353.15	22.25	$Mg(H_2PO_2)_2$
298.15	11.69	S_1	363.15	21.99	$Mg(H_2PO_2)_2$
303.15	13.14	S_1	373.15	21.61	$Mg(H_2PO_2)_2$
313.15	16.72	S_1	375.65[c]	21.34	$Mg(H_2PO_2)_2$

[a] Standard uncertainties: $u(T) = 0.05$ K, $u(P) = 0.2$ kPa, $u_r(x)$ for $Mg(H_2PO_2)_2$ is 0.5%.
[b] S_1: $Mg(H_2PO_2)_2 \cdot 6H_2O$.
[c] Boiling point.