

Solid–liquid phase equilibria of $\text{Ca}(\text{H}_2\text{PO}_2)_2\text{--CaCl}_2\text{--H}_2\text{O}$ and $\text{Ca}(\text{H}_2\text{PO}_2)_2\text{--NaH}_2\text{PO}_2\text{--H}_2\text{O}$ ternary systems at 298.15 K



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ABSTRACT

Calcium hypophosphite has been widely used as an anti-corrosive agent, flame retardant, fertilizer, assistant for Ni electroless plating, and animal nutrition supplements. High purity calcium hypophosphite can be synthesized via the replacement reaction of sodium hypophosphite and calcium chloride. In this work, the solid–liquid phase equilibria of $\text{Ca}(\text{H}_2\text{PO}_2)_2\text{--CaCl}_2\text{--H}_2\text{O}$ and $\text{Ca}(\text{H}_2\text{PO}_2)_2\text{--NaH}_2\text{PO}_2\text{--H}_2\text{O}$ ternary systems at 298.15 K were studied experimentally via the classical isothermal solubility equilibrium method, and the phase diagrams for these two systems were obtained. It was found that two solid salts of $\text{Ca}(\text{H}_2\text{PO}_2)_2$ and $\text{CaCl}_2\cdot 6\text{H}_2\text{O}$, and three solid salts of $\text{Ca}(\text{H}_2\text{PO}_2)_2$, $\text{NaCa}(\text{H}_2\text{PO}_2)_3$, and $\text{NaH}_2\text{PO}_2\cdot\text{H}_2\text{O}$ can form in the corresponding systems under phase-equilibrium conditions. $\text{Ca}(\text{H}_2\text{PO}_2)_2$ has low solubility in the $\text{Ca}(\text{H}_2\text{PO}_2)_2\text{--CaCl}_2\text{--H}_2\text{O}$ system. $\text{NaCa}(\text{H}_2\text{PO}_2)_3$ occupies a large solid field in the ternary system of $\text{Ca}(\text{H}_2\text{PO}_2)_2\text{--NaH}_2\text{PO}_2\text{--H}_2\text{O}$.

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1. Introduction

Calcium hypophosphite is widely used as an anti-corrosive agent, flame retardant, fertilizer, assistant for Ni electroless plating and animal nutrition supplements [1]. Owing to its high reducibility, calcium hypophosphite is typically used instead of hypophosphorous acid as a mild deamination reagent [2]. In addition, calcium hypophosphite is used for treating obesity in humans [3].

Calcium hypophosphite is synthesized via a phosphorus sludge processing with alkali, according to the following equation (8) $\text{P} + 3\text{Ca}(\text{OH})_2 + 6\text{H}_2\text{O} = 3\text{Ca}(\text{H}_2\text{PO}_2)_2 + 2\text{PH}_3$. However, this synthesis is accompanied by the production of waste, namely phosphite-containing slag (a mixture of CaHPO_3 and CaCO_3), which amounts to about 25% of the yellow phosphorus remnants [4]. To obtain a higher purity of calcium hypophosphite for specific applications, the following replacement reaction was employed: $\text{CaCl}_2 + 2\text{NaH}_2\text{PO}_2\cdot\text{H}_2\text{O} = \text{Ca}(\text{H}_2\text{PO}_2)_2 + 2\text{NaCl} + 2\text{H}_2\text{O}$.

Solid–liquid phase equilibria (SLE) data and phase diagrams are essential for process development, design and control. SLE data of H_2PO_2^- -containing systems that relate to hydrometallurgy have been reported, such as, the several ternary systems of $\text{Na}_2(\text{H}_2\text{PO}_2)_2\text{--Mn}(\text{H}_2\text{PO}_2)_2\text{--H}_2\text{O}$, $\text{Ca}(\text{H}_2\text{PO}_2)_2\text{--Mn}(\text{H}_2\text{PO}_2)_2\text{--H}_2\text{O}$

$(\text{NH}_4)_2(\text{H}_2\text{PO}_2)_2\text{--Mn}(\text{H}_2\text{PO}_2)_2\text{--H}_2\text{O}$ at 293.15 K by R.M. Dolinina et al. [5]; $\text{NaH}_2\text{PO}_2\text{--Ba}(\text{H}_2\text{PO}_2)_2\text{--H}_2\text{O}$, $\text{NaCl--NaH}_2\text{PO}_2\text{--H}_2\text{O}$, and $\text{BaCl}_2\text{--Ba}(\text{H}_2\text{PO}_2)_2\text{--H}_2\text{O}$ at 273.15 K by Erge et al. [6]; $\text{NaH}_2\text{PO}_2\text{--Zn}(\text{H}_2\text{PO}_2)_2\text{--H}_2\text{O}$, $\text{NaCl--NaH}_2\text{PO}_2\text{--H}_2\text{O}$, and $\text{ZnCl}_2\text{--Zn}(\text{H}_2\text{PO}_2)_2\text{--H}_2\text{O}$ at 273.15 K by Adiguzel et al. [7].

Several quaternary systems of H_2PO_2^- -containing have been reported, for example $\text{Na}^+\text{--Mn}^{2+}/\text{Cl}^-\text{--}(\text{H}_2\text{PO}_2)^-\text{--H}_2\text{O}$ at 293.15 K by Aliev [8]; $\text{Na}^+\text{--Mn}^{2+}/\text{NO}_3^-\text{--}(\text{H}_2\text{PO}_2)^-\text{--H}_2\text{O}$ at 273.15 K by Alisoglu and Necefoglu [9]; $\text{Na}^+\text{--Mn}^{2+}/\text{Cl}^-\text{--}(\text{H}_2\text{PO}_2)^-\text{--H}_2\text{O}$ [10] and $\text{K}^+\text{--Mn}^{2+}/\text{Br}^-\text{--}(\text{H}_2\text{PO}_2)^-\text{--H}_2\text{O}$ [11] at 298.15 K by Alisoglu; $\text{Na}^+\text{--Mn}^{2+}/\text{Br}^-\text{--}(\text{H}_2\text{PO}_2)^-\text{--H}_2\text{O}$ at 278.15 K by Alisoglu et al. [12]; $\text{Na}^+\text{--Ba}^{2+}/\text{Cl}^-\text{--}(\text{H}_2\text{PO}_2)^-\text{--H}_2\text{O}$ and $\text{Na}^+\text{--Zn}^{2+}/\text{Cl}^-\text{--}(\text{H}_2\text{PO}_2)^-\text{--H}_2\text{O}$ at 273.15 K by Erge et al. [6] and Adiguzel et al. [7].

However, SLE data for $\text{Ca}^{2+}\text{--Na}^+/\text{Cl}^-\text{--}(\text{H}_2\text{PO}_2)^-\text{--H}_2\text{O}$ system and its subsystems are scant, except for the subsystem of $\text{NaCl--CaCl}_2\text{--H}_2\text{O}$ [13]. In this study, we focused on the solid–liquid phase equilibria of $\text{Ca}(\text{H}_2\text{PO}_2)_2$ -containing ternary systems of $\text{Ca}(\text{H}_2\text{PO}_2)_2\text{--CaCl}_2\text{--H}_2\text{O}$ and $\text{Ca}(\text{H}_2\text{PO}_2)_2\text{--NaH}_2\text{PO}_2\text{--H}_2\text{O}$; we also report their SLE data and phase diagrams at 298.15 K.

2. Experimental

2.1. Apparatus and reagents

The chemicals used in this study were purified before use; these are described in Table 1. Doubly deionized water with conductivity

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Table 1
Chemical samples used in this study.

Chemical	CAS no.	Source	Initial mass fraction purity	Purification method	Final mass fraction purity	Analysis method
Calcium chloride anhydrous	10043-52-4	A.R. ^a	0.960	Recrystallization	0.995 ^b	EDTA method for Ca ²⁺ and AgNO ₃ method for Cl ⁻
Calcium hypophosphite	7789-79-9	A.R. ^a	0.990	None	0.990	EDTA method for Ca ²⁺ and Na ₂ S ₂ O ₃ method for H ₂ PO ₂ ⁻
Sodium hypophosphite	7681-51-0	A.R. ^a	0.990	None	0.990	Na ₂ S ₂ O ₃ method for H ₂ PO ₂ ⁻

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^b Record by CaCl₂·6H₂O.

lower than $1 \times 10^{-4} \text{ S m}^{-1}$ and pH of 6.60 at 298.15 K was used to prepare the solid-liquid mixtures employed for the experiments and chemical analysis.

The solid-liquid phase equilibria measurements of the Ca(H₂PO₂)₂-CaCl₂-H₂O and Ca(H₂PO₂)₂-NaH₂PO₂-H₂O ternary systems were carried out in a jacketed equilibrium tank (Chemglass Scientific Apparatus, 2000 mL) with a mechanical stirrer (Heidolph). The temperature of the solid-liquid mixtures was controlled by a thermostatic oil bath (Huber K6s-cc-NR) and measured with a mercury-in-glass thermometer with an accuracy of $\pm 0.05 \text{ K}$.

2.2. Experimental

The isothermal solubility equilibrium methodology was adopted to determine the SLE data. For example, in order to study the Ca(H₂PO₂)₂ saturated solid-liquid mixture of the Ca(H₂PO₂)₂-CaCl₂-H₂O system, an initial solid-liquid mixture with 100 g water and 100 g calcium hypophosphite was prepared. A given amount of CaCl₂·6H₂O was then added to the mixture at different stages until the invariant point was found. During the entire experimental procedure, the mixture was kept at a temperature of 298.15 K; at each stage, the mixture was stirred for at least one day until stabilization was reached; it was then allowed to settle for at least 4 h or until the liquid phase became completely clear. The liquid samples and wet solid samples were taken through the top port and bottom valve, respectively; the wet solid samples were separated by isothermal filtration. The initial solid-liquid mixture of saturated CaCl₂ was prepared by using 50 g water, and 550 g CaCl₂·6H₂O; Ca(H₂PO₂)₂ was then added at different stages, until the invariant point was found. For the Ca(H₂PO₂)₂-NaH₂PO₂-H₂O system, the same procedure with the initial solid-liquid mixtures of 100 g Ca(H₂PO₂)₂+250 g water, and 400 g NaH₂PO₂·H₂O+200 g water were used to determine the Ca(H₂PO₂)₂ and NaH₂PO₂ saturation curves, respectively.

The liquid and wet solid samples were studied by chemical analysis, and then, the wet solid sample was further disposed by drying with filter paper and studied using X-ray powder diffractometer (XRD)(PERSEE, XD-3). The density of the liquid phase was measured using an isothermal densimeter (METTLER DE51) with a precision temperature of $\pm 0.02 \text{ K}$ and a standard uncertainty density of less than $\pm 0.0001 \text{ kg L}^{-1}$.

2.3. Analytical methods

The weighted samples were placed in a 250 ml volumetric flask, dissolved in water, and diluted to the total volume. The concentrations of Ca²⁺ and Cl⁻ were analyzed via complexometric titration with EDTA [14], and Mohr titration with AgNO₃ [14], respectively. To determine the H₂PO₂⁻ ion concentration, an improved iodometry method was used. In particular, 2–5 mL sample was mixed with 25 ml (KBrO₃ + KBr) solution (0.1 mol L⁻¹), and 5 ml H₂SO₄ solution (2.0 mol L⁻¹) in a closed iodine flask. The mixture was then settled in a dark place for 1 h and kept at a temperature higher than 298.15 K. Iodine formed in the reaction was titrated using a Na₂S₂O₃-water standard solution (0.1 mol L⁻¹) with an indicator of 5.0 g L⁻¹ starch in water. Before titration, an excess amount (about 5 ml) KI solution (200 g L⁻¹) was added, and then, the solution was shaken and settled for 10 min. Parallel blank experiments were carried out. In particular, the concentration of the Na⁺ ion was calculated by electroneutrality, and that of the H₂PO₂⁻ ion concentration was calculated using the following equation:

$$\text{H}_2\text{PO}_2^- = \frac{(V_1 - V_2) \times c \times M \times V_4 \times 100}{1000 \times V_3 \times m} \quad (1)$$

where, V_{1-2} are the volumes of the Na₂S₂O₃ standard solution for the blank experiment and sample titration; V_{3-4} are the sample

Table 2
Solid-liquid equilibria data for the Ca(H₂PO₂)₂-CaCl₂-H₂O ternary system at $T = 298.15 \text{ K}$ and $p = 101.3 \text{ kPa}$.^a

No.	Liquid phase (% mass)			Density ($\rho/\text{kg L}^{-1}$)	Wet solid (% mass)			Solid phase ^b
	Ca(H ₂ PO ₂) ₂	CaCl ₂	H ₂ O		Ca(H ₂ PO ₂) ₂	CaCl ₂	H ₂ O	
1	13.89	0.00	86.11	1.0912	75.60	0.00	24.40	S ₁
2	8.37	11.74	79.89	1.1560	69.73	4.07	26.20	S ₁
3	5.86	21.51	72.63	1.2296	72.77	5.87	21.36	S ₁
4	4.95	29.80	65.25	1.3052	71.25	8.99	19.76	S ₁
5	4.79	36.73	58.48	1.3841	72.14	10.91	16.95	S ₁
6	5.92	42.5	51.58	1.4591	71.22	13.24	15.54	S ₁
7	6.23	44.87	48.90	1.4921	11.92	43.53	44.55	S ₁ +S ₂
8	6.23	44.87	48.90	1.4921	25.93	37.04	37.03	S ₁ +S ₂
9	6.09	44.68	49.23	1.4881	1.03	49.88	49.09	S ₂
10	3.24	44.52	52.24	1.4675	1.02	48.5	50.48	S ₂
11	0.00	44.33	55.67	1.4448	0.00	48.52	51.48	S ₂

^a Standard uncertainties u are $u(T) = 0.05 \text{ K}$, $u(p) = 0.2 \text{ kPa}$ (ambient pressure change), $u(\rho) = 0.0001 \text{ kg L}^{-1}$, $u(x)$ for Ca(H₂PO₂)₂, CaCl₂ are 0.0002 and 0.0002 in mass fraction, respectively.

^b S₁: Ca(H₂PO₂)₂, S₂: CaCl₂·6H₂O.

Table 3
Solid–liquid equilibria data for the $\text{Ca}(\text{H}_2\text{PO}_2)_2$ – NaH_2PO_2 – H_2O ternary system at $T=298.15\text{ K}$ and $p=101.3\text{ kPa}$.^a

No.	Liquid phase (% mass)			Density ($\rho/\text{kg L}^{-1}$)	Wet solid (% mass)			Solid phase ^b
	$\text{Ca}(\text{H}_2\text{PO}_2)_2$	NaH_2PO_2	H_2O		$\text{Ca}(\text{H}_2\text{PO}_2)_2$	NaH_2PO_2	H_2O	
1	13.89	0.00	86.11	1.0912	88.60	0.00	11.40	S ₁
2	8.63	5.04	86.33	1.0914	72.03	1.50	26.47	S ₁
3	5.24	10.94	83.82	1.1064	71.30	3.20	25.50	S ₁
4	3.05	16.18	80.77	1.1555	70.64	4.60	24.76	S ₁
5	3.03	16.54	80.43	1.1837	65.06	9.12	25.82	S ₁ + S ₃
6	3.03	16.54	80.43	1.1837	59.46	13.15	27.39	S ₁ + S ₃
7	3.03	16.54	80.43	1.1837	53.50	18.79	27.71	S ₁ + S ₃
8	0.80	23.90	75.30	1.1705	44.90	30.45	24.65	S ₃
9	0.09	35.05	64.86	1.2495	42.97	34.26	22.77	S ₃
10	0.03	43.53	56.44	1.3193	41.70	37.23	21.07	S ₃
11	0.03	47.41	52.56	1.3422	43.47	38.35	18.18	S ₃
12	0.03	51.49	48.48	1.3805	29.76	48.31	21.93	S ₃ + S ₄
13	0.03	51.49	48.48	1.3805	9.84	64.59	25.57	S ₃ + S ₄
14	0.00	51.95	48.05	1.3790	0.00	78.01	21.99	S ₄

^a Standard uncertainties u are $u(T)=0.05\text{ K}$, $u(p)=0.2\text{ kPa}$ (ambient pressure change), $u(\rho)=0.0001\text{ kg L}^{-1}$. $u(x)$ for $\text{Ca}(\text{H}_2\text{PO}_2)_2$, NaH_2PO_2 are 0.00006 and 0.0001 in mass fraction, respectively.

^b S₁: $\text{Ca}(\text{H}_2\text{PO}_2)_2$, S₃: $\text{NaCa}(\text{H}_2\text{PO}_2)_3$, S₄: $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$.

and dilute volumes; c is the concentration of the $\text{Na}_2\text{S}_2\text{O}_3$ standard solution; m is the weight of liquid or solid sample; M ($=16.25\text{ g mol}^{-1}$) is a constant which equates to the quarter of the molecular mass of H_2PO_2^- .

3. Results and discussion

The salt solubility of the binary salt–water systems was measured to be 44.33% mass CaCl_2 , 51.95% mass NaH_2PO_2 , and 13.89% mass $\text{Ca}(\text{H}_2\text{PO}_2)_2$ at 298.15 K; the corresponding solids are $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ and $\text{Ca}(\text{H}_2\text{PO}_2)_2$, respectively.

The solid–liquid phase equilibria data of the ternary systems of $\text{Ca}(\text{H}_2\text{PO}_2)_2$ – CaCl_2 – H_2O and $\text{Ca}(\text{H}_2\text{PO}_2)_2$ – NaH_2PO_2 – H_2O are given in Tables 2 and 3, along with the wet-solid data and corresponding liquid densities. The characteristics of the solid–liquid phase equilibria of the two ternary systems are shown in Figs. 1 and 2, respectively. The solubility–density graphics are shown in Fig. 3.

For the $\text{Ca}(\text{H}_2\text{PO}_2)_2$ – CaCl_2 – H_2O system, our results showed that the solid salts of $\text{Ca}(\text{H}_2\text{PO}_2)_2$ (S₁) and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (S₂) are in equilibrium with liquid phase. The invariant point (B in Fig. 1) of co-saturated $\text{Ca}(\text{H}_2\text{PO}_2)_2$ and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ was determined to be 6.23% mass $\text{Ca}(\text{H}_2\text{PO}_2)_2$, 44.87% mass CaCl_2 , and 48.90% mass

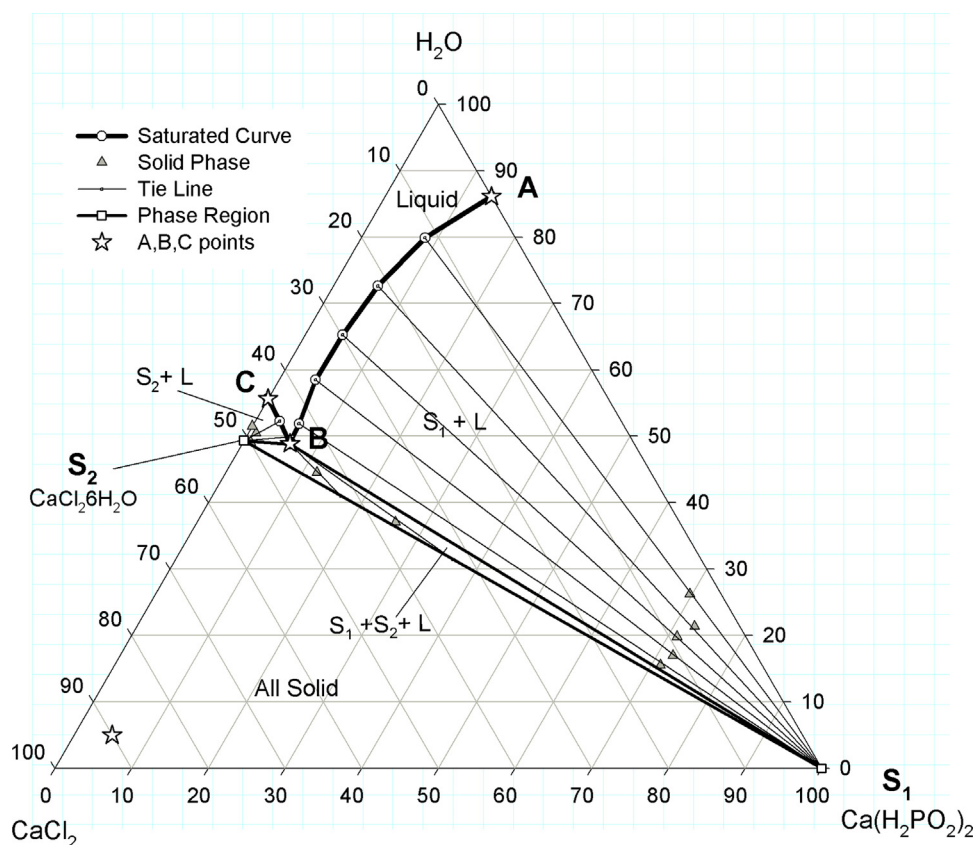


Fig. 1. Solubility diagram of the $\text{Ca}(\text{H}_2\text{PO}_2)_2$ – NaH_2PO_2 – H_2O system at 298.15 K.

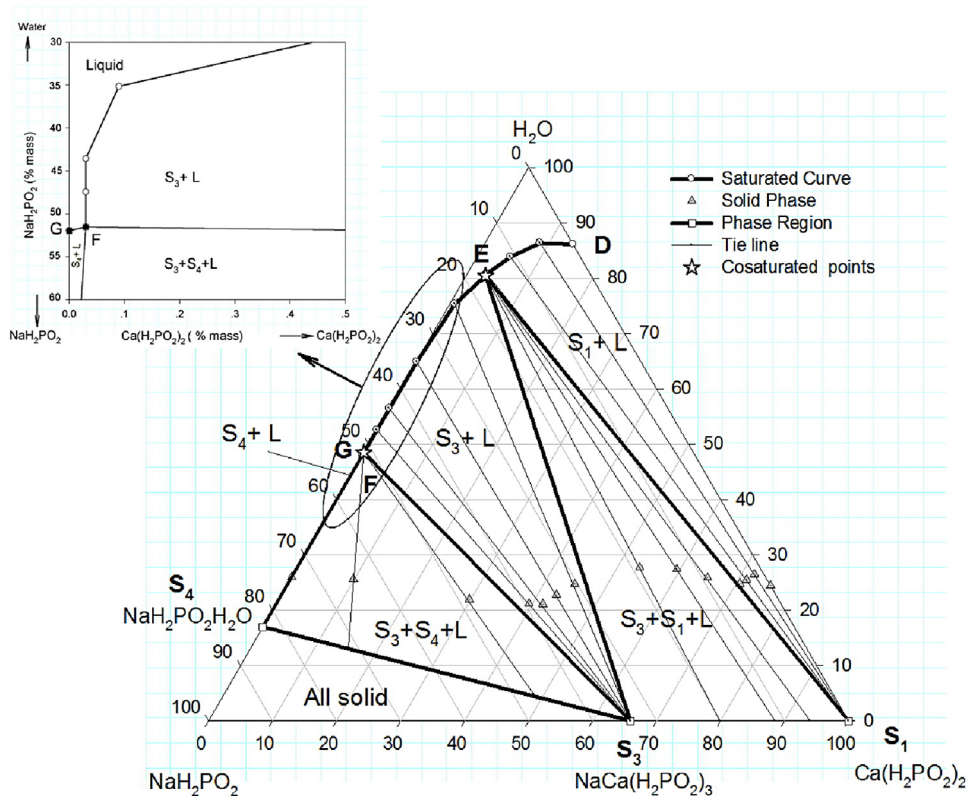


Fig. 2. Solubility diagram of the $\text{Ca}(\text{H}_2\text{PO}_2)_2$ - NaH_2PO_2 - H_2O system at 298.15 K.

water, with the liquid density of the invariant point being 1.4921 kg L^{-1} .

Data displayed in Table 2 and Fig. 1 suggest that the $\text{Ca}(\text{H}_2\text{PO}_2)_2$ solubility is lower than that of CaCl_2 ; this results in a significantly larger solid region of $\text{Ca}(\text{H}_2\text{PO}_2)_2$ compared to that of CaCl_2 . The

densities of the saturated liquids are affected by the composition of the contained salts, with the largest density being found at the invariant point.

For the $\text{Ca}(\text{H}_2\text{PO}_2)_2$ - NaH_2PO_2 - H_2O system, (Table 3 and Fig. 2), besides the solid salts of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ (S_4) and $\text{Ca}(\text{H}_2\text{PO}_2)_2$ (S_1), an

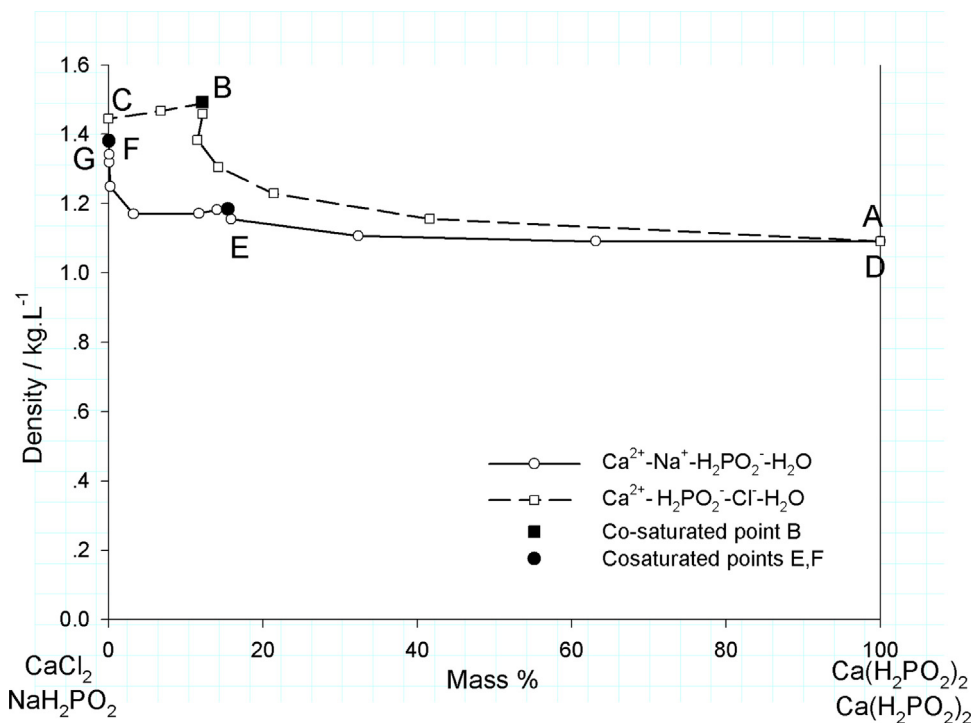


Fig. 3. Density diagram for the ternary systems $\text{Ca}(\text{H}_2\text{PO}_2)_2$ - NaH_2PO_2 - H_2O and $\text{Ca}(\text{H}_2\text{PO}_2)_2$ - CaCl_2 - H_2O at $T=298.15 \text{ K}$ and $p=101.3 \text{ kPa}$.

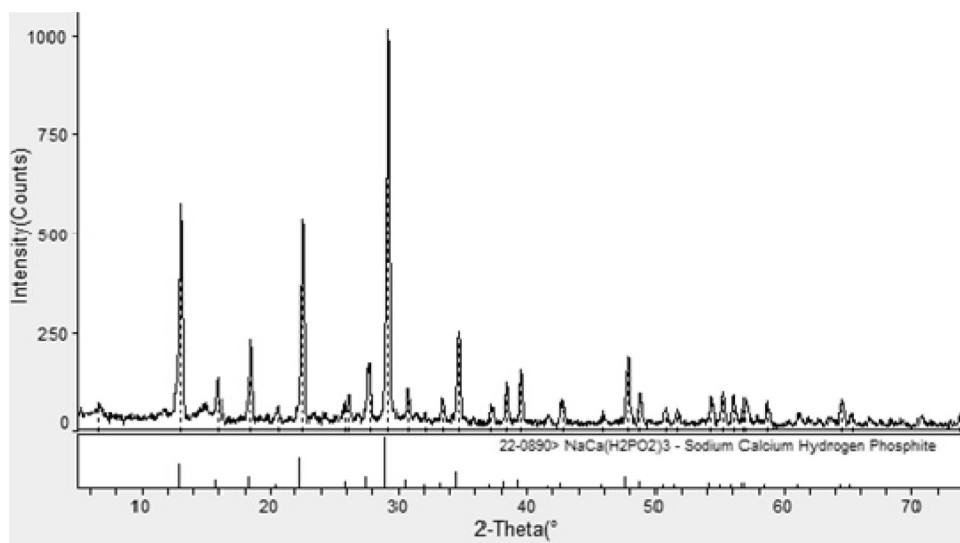


Fig. 4. XRD pattern of no.8–11 solid samples listed in Table 2.

anhydrous double salt, $\text{NaCa}(\text{H}_2\text{PO}_2)_3$ (S_3), is found in the system; XRD analysis is shown in Fig. 4. One incommensurate invariant point E ($S_1 + S_3$) and one commensurate invariant point F ($S_3 + S_4$) are determined as 3.03% mass $\text{Ca}(\text{H}_2\text{PO}_2)_2$ and 16.54% mass of NaH_2PO_2 , and 0.03% and 51.49%, respectively. The densities of the invariant points are 1.1837 kg L^{-1} and 1.3805 kg L^{-1} for B and C, respectively.

The data in Fig. 2 indicate that the complex salt of $\text{NaCa}(\text{H}_2\text{PO}_2)_3$ is an incompatible double-salt which decomposes into the $\text{Ca}(\text{H}_2\text{PO}_2)_2$ solid salt and a NaH_2PO_2 -containing solution upon water addition. The co-saturated point F has a trace solubility of $\text{Ca}(\text{H}_2\text{PO}_2)_2$ which makes it very close to point G (NaH_2PO_2 saturated in water). The local enlargement of Fig 2 shows the details of F and G. $\text{NaCa}(\text{H}_2\text{PO}_2)_3$ occupies a large region in the ternary phase diagram, suggesting that it can be easily formed upon the addition of $\text{Ca}(\text{H}_2\text{PO}_2)_2$ to the NaH_2PO_2 -containing solution.

4. Conclusion

The solid–liquid phase equilibria of the $\text{Ca}(\text{H}_2\text{PO}_2)_2$ – CaCl_2 – H_2O and $\text{Ca}(\text{H}_2\text{PO}_2)_2$ – NaH_2PO_2 – H_2O ternary systems at 298.15 K were studied using the isothermal solubility equilibrium method, and their phase diagrams and density were obtained. It was found that two solid salts of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ca}(\text{H}_2\text{PO}_2)_2$, and three solid salts of $\text{Ca}(\text{H}_2\text{PO}_2)_2$, $\text{NaCa}(\text{H}_2\text{PO}_2)_3$, and $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ can be formed in the corresponding systems under phase equilibrium conditions. $\text{Ca}(\text{H}_2\text{PO}_2)_2$ has low solubility in the $\text{Ca}(\text{H}_2\text{PO}_2)_2$ – CaCl_2 – H_2O system; $\text{NaCa}(\text{H}_2\text{PO}_2)_3$ occupies a large solid field in the ternary phase diagram of $\text{Ca}(\text{H}_2\text{PO}_2)_2$ – NaH_2PO_2 – H_2O .

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