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Solid-liquid phase equilibrium for the system ammonium polyphosphate-urea ammonium nitrate-potassium chloride-water at 273.2 K

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ABSTRACT

Based on the dynamic method, a quaternary system of ammonium polyphosphate (APP)-urea ammonium nitrate (UAN, $CO(NH_2)_2$-NH_4NO_3)-potassium chloride (KCl)-H_2O and its subsystems (APP-[$CO(NH_2)_2$-NH_4NO_3]-H_2O, KCl-[$CO(NH_2)_2$-NH_4NO_3]-H_2O and APP-KCl-H_2O) were systematically investigated at the temperature of 273.2 K. Each ternary phase diagram contains one invariant point and three crystallization regions. The crystallization regions are: (1) $(NH_4)_3HP_2O_7$, $(NH_4)_4P_2O_7$ and ($(NH_4)_3HP_2O_7$ + $(NH_4)_4P_2O_7$) for APP-[$CO(NH_2)_2$-NH_4NO_3]-H_2O diagram; (2) KCl, KNO_3 and (KCl + KNO_3) for KCl-[$CO(NH_2)_2$-NH_4NO_3]-H_2O diagram and (3) $(NH_4)_3HP_2O_7$, KCl and ($(NH_4)_3HP_2O_7$ + KCl) for APP-KCl-H_2O diagram. The quaternary phase diagram of APP-[$CO(NH_2)_2$-NH_4NO_3]-KCl-H_2O has no quaternary invariant point but includes four solid phase crystallization regions, *i.e.*, $(NH_4)_3HP_2O_7$, $(NH_4)_4P_2O_7$, KNO_3 and KCl, in which the KNO_3 region occupies the largest area. The maximum total nutrient content (N + P_2O_5 + K_2O) existing as ionic forms in the APP-[$CO(NH_2)_2$-NH_4NO_3]-H_2O, KCl-[$CO(NH_2)_2$-NH_4NO_3]-H_2O, APP-KCl-H_2O and quaternary systems is 44.70%, 32.86%, 45.56% and 46.23% (mass), respectively, indicating that the maximum nutrient content can be reached using raw materials of the corresponding systems to prepare liquid fertilizer. In the quaternary system, the content of NH_4^+-N ascends with the increase of the total nutrient content, while the contents of NO_3^--N and $CO(NH_2)_2$-N increase with elevated total N. This work can help optimize the operating parameters for the production, storage and transportation of liquid fertilizers.

1. Introduction

As a significant fertilizer, water-soluble ammonium polyphosphate (APP) is generally used as a basal P source in combination with other nutrients (N, K, Zn, Mg, *etc.*) during a practical fertilization [1–6]. The producing processes of water-soluble APP have two main types of phosphoric acid (PA) ammoniation and ammonium phosphate (AP)-urea condensation [7,8]. As early as 1960s, Tennessee Valley Authority (TVA) [9] successfully manufactured the water-soluble APP with appropriate polymerization degree distribution using PA ammoniation method [7]. Water-soluble APP had been widely used in developed countries such as Europe and America, and the output of water-soluble APP in the United States exceeded 2 million tons annually [10]. The common fertilizer grades for water-soluble APP are 11-37-0 (*i.e.*, 11% (mass) N, 37% (mass) P_2O_5 and 0% (mass) K_2O in the fertilizer), 8-24-0 and 10-34-0. However, the fore mentioned water-soluble APPs are aquiferous, which need to be stored at a relatively low temperature for hydrolysis resistance [11]. Moreover, water-contained products could require more input in transportation than corresponding granules, due to solution's lower nutrient content. Hence, a new kind of solid water-soluble APP has been produced through AP-urea method in China [8]. The grade of this APP is 18-58-0 with 77% of phosphorus as pyrophosphate [12], providing expected prospects for its transportation convenience.

Phase diagram plays an important role in guiding the application of water-soluble APP in agriculture. In the 1950s Slack *et al.* [13] explored the quaternary systems' solubility of $CO(NH_2)_2$-NH_3-H_3PO_4-KCl-H_2O with fixed NH_3-H_3PO_4 molar ratios of 1.5,

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1.6 and 1.7, NH_4NO_3-NH_3-H_3PO_4-KCl-H_2O with fixed NH_3-H_3PO_4 molar ratio of 1.7, and [$CO(NH_2)_2$-NH_4NO_3](UAN)–NH_3-H_3PO_4-KCl-H_2O with fixed $CO(NH_2)_2$-NH_4NO_3 mole ratio of 1.1 or fixed NH_3-H_3PO_4 mole ratio of 1.7 at 273.2 K. These quaternary systems contain up to 37% (mass) total plant-nutrient (TPN = N + P_2O_5 + K_2O). Subsequently, APP (10-34-0) and APP(11-37-0) were produced by using the superphosphoric acid containing 76% and 78%–80% P_2O_5, respectively, and the quaternary phase diagrams of the APP(10-34-0)-[$CO(NH_2)_2$-NH_4NO_3](UAN)-KCl-H_2O and APP (11-37-0)-UAN-KCl-H_2O were measured at 273.2 K, which can reach 45% (mass) [9] and 49% (mass) [11] TPN, respectively. Based on the aforementioned quaternary systems, the equations were established to calculate the change of TPN content under different temperatures. The hard-earned data enlightened the regularity of solubility of polyphosphates under different ammoniation degrees. In addition, some derivative systems have been also exploited. Joseph *et al.* [14] studied the solubility of $CO(NH_2)_2$-NH_3-H_3PO_4-$H_4P_3O_7$-$H_5P_3O_{10}$-H_2O at 273.2 and 298.2 K. Leonov *et al.* [15] has tried on the NH_4NO_3-$NH_4H_2PO_4$-$CO(NH_2)_2$-KCl system and the hygroscopic trend of the quaternary system was obtained. Based on the same reason of producing high-analysis liquid fertilizer, the comprehensive solubility study for phosphoric acid and ammonium thiosulfate in urea ammonium nitrate mixtures were performed [16,17]. Kaddami *et al.* [18,19] measured the ternary system $NH_4H_2PO_4$-$(NH_4)_2HPO_4$-H_2O to specify a metastable equilibrium of these phosphates at 264.2, 266.2, 303.2, 318.2 and 338.2 K, respectively.

However, as a new type of solid water-soluble APP, APP(18-58-0) is quite different to draw lessons from the above thermodynamic systems just involving liquid APP(10-34-0, 11-37-0), which confined the Granular APP's application. Since the phase equilibrium of APP(18-58-0)-$NH_4H_2PO_4$-$(NH_4)_2HPO_4$-H_2O system at 298.2 K accomplished in our previous work has opened the prelude of solid-APP dissolution [20], the phase diagram of APP(18-58-0)-[$CO(NH_2)_2$-NH_4NO_3]-KCl-H_2O quaternary system comes at the appointed time, herein. This work can help optimize the operating parameters for the production, storage and transportation of APP contained liquid fertilizers.

2. Experimental

2.1. Materials

The experimental materials of water-soluble solid APP(18-58-0) and UAN were provided by Guizhou Chuanheng Chemical Corp. and Jinkai Investment Holding Group., China with the purity of 98.8% (mass) and 99.6% (mass), respectively. As shown in Fig. 1, the P in APP(18-58-0) consists of 23% (mass) of orthophosphate and 77% (mass) of pyrophosphate, which were determined by an ion-chromatography method [21]. The contents of ammonium nitrogen (NH_4^+-N) and phosphorus pentoxide (P_2O_5) of APP(18-58-0) are 18.93% (mass) and 58.59% (mass), respectively. For convenience, APP(18-58-0) was referred to as APP thereafter. UAN solution with 32.79% (mass) N consists of 36.11% (mass) $CO(NH_2)_2$, 45.60% (mass) NH_4NO_3 and 18.25% (mass) H_2O. The mass fraction of NH_4^+-N, nitrate nitrogen (NO_3^--N) and urea nitrogen ($CO(NH_2)_2$-N) of UAN are 7.95% (mass), 7.99% (mass) and 16.85% (mass), respectively. Analytical pure KCl was purchased from Jinshan Chemical Test, with a purity of 99.5% (mass). All reagents were used without further purification and the water used in this work was deionized water with specific conductivity of 0.055 $\mu S\cdot cm^{-1}$.

2.2. Apparatus and procedures

The dynamic method was adopted to study the solid–liquid phase equilibrium in this work [22–25]. The experimental equipment for the measurement of solubility, was in accordance with the previous work [26]. The experiment apparatus of solubility measurement is shown in Fig. 2. The solubility of quaternary system (APP-[$CO(NH_2)_2$-NH_4NO_3]-KCl-H_2O) was measured as follows: (1) The UAN-water solution of known mass and composition was firstly added to the jacket beaker (250 ml), and was controlled at (273.2±0.1) K by a thermostatic water bath (DFY-10L/20, Gongyi Yuhua Instrument Co., Ltd, China) by using mercury thermometer to detect the solution's temperature with uncertainty of ±0.01 K. A magnetic stirrer (B4-1A, Shanghai Sile Instrument Co., Ltd, China) was used to provide vigorous agitation for homogeneous mixing and quick equilibrium. (2) According to the preset mass fraction of K_2O from 0% to 3.10%, a known weigh of KCl was put into the solution and dissolved completely. (3) A known weigh of APP was slowly added into the solution. If the added APP dissolved, a known weighted APP was added again. Until the added APP was not dissolved in the solution with continuous stirring for about 1 h and the new crystal was slowly formed, the solid–liquid phase diagram equilibria were established.

As for realizing the mass fraction of K_2O is over 3.10%. (1) A certain little amount of APP was first added to the UAN-H_2O solution of known composition. (2) Until the added APP fully dissolved, a known weigh of KCl was put into the solution. (3) A small amount of weighed KCl was added again if the added KCl was dissolved. Until the added KCl was not dissolved in the solution with continuous stirring for about 1 h. The solid–liquid phase equilibria were reached. The mixture was kept in the thermostatic water bath

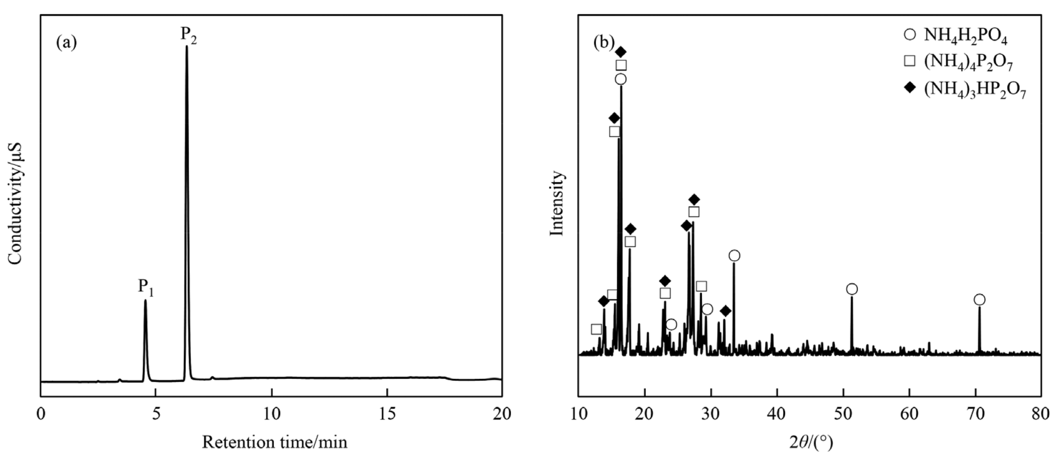

Fig. 1. The polymerization degree distribution of ammonium polyphosphate (a) (P_1, orthophosphate; P_2, pyrophosphate) and X-ray diffraction pattern of APP (b).

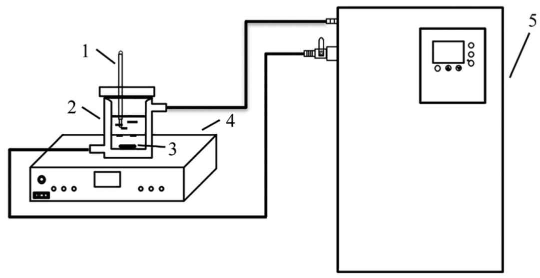

Fig. 2. The experiment apparatus of solubility measurement (1. Mercury thermometer; 2. Jacketed beaker; 3. Magnetic rotor; 4. Magnetic stirring apparatus; 5. Thermostatic water bath).

without stirring for at least 1 h to settle down solids. The density (ρ) of supernatant with different composition was determined *via* a 10 ml pycnometer with uncertainty of 0.0002 $g\cdot cm^{-3}$ [27,28]. All of the additions were weighed by an analytical balance (AL104, Mettler Toledo, USA) with an uncertainty of ± 0.0001 g. Finally, the solid phase was vacuum filtered, freeze-dried for more than 8 h at 253.2 K for X-ray diffraction (XRD, X'Pert PRO, PANalytical B.V., Netherlands) analysis.

The total addition of UAN, APP and KCl before the last additions of APP or KCl was the solubility of phase equilibrium systems. The content of N, P_2O_5 and K_2O in mass fraction in the saturated solution are given as:

$$w_{\mathrm{N}} = \frac{m_1 \times 0.1893 + m_2 \times 0.3279}{m} \times 100\% \tag{1}$$

$$w_{\mathrm{P_2O_5}} = \frac{m_1 \times 0.5859}{m} \times 100\% \tag{2}$$

$$w_{\mathrm{K_2O}} = \frac{m_3 \times 0.6318}{m} \times 100\% \tag{3}$$

$$w_{\mathrm{NH_4^+-N}} = \frac{m_1 \times 0.1893 + m_2 \times 0.0795}{m} \times 100\% \tag{4}$$

$$w_{\mathrm{NO_3^--N}} = \frac{m_2 \times 0.0799}{m} \times 100\% \tag{5}$$

$$w_{\mathrm{CO(NH_2)_2-N}} = \frac{m_2 \times 0.1685}{m} \times 100\% \tag{6}$$

$$w_{\mathrm{H_2O}} = \frac{m_2 \times 0.1825 + m_4}{m} \times 100\% \tag{7}$$

where $m = m_1 + m_2 + m_3 + m_4$; m_1, m_2, m_3, m_4 represent the masses of APP, UAN, KCl and H_2O in the saturated solution, respectively; 0.0795, 0.0799, 0.1685, 0.3279, 0.1825 are the mass fractions of NH_4^+-N, NO_3^--N, $CO(NH_2)_2$-N, total N and H_2O in UAN, respectively; 0.6318, 0.1893, 0.5859 are the mass fractions of K_2O in KCl, NH_4^+-N, P_2O_5 in APP, respectively.

3. Results and Discussion

3.1. Solid-liquid equilibrium of APP-[$CO(NH_2)_2$-NH_4NO_3]–H_2O

The solubility of the ternary system APP-[$CO(NH_2)_2$-NH_4NO_3]–H_2O at 273.2 K was measured and the data are presented in Table 1. UAN is one of the important nitrogen sources and the mass ratio of $CO(NH_2)_2$ and NH_4NO_3 (*i.e.*, $\omega(CO(NH_2)_2)/\omega(NH_4NO_3)$) in the UAN solution is fixed at 0.8. Thus, the solute of $CO(NH_2)_2$ and NH_4NO_3 in UAN solution is discussed. As shown in Fig. 3, it can be seen that the isothermal solubility diagram contains one invariant point C_1, two single crystallization zones (I_1, II_1), one eutectic crystallization zone (III_1) and two solubility curves (E_1C_1 and C_1F_1, corresponding to the crystallization of triammonium pyrophosphate ($(NH_4)_3HP_2O_7$), ammonium pyrophosphate ($(NH_4)_4P_2O_7$). The invariant point C_1 is saturated with $(NH_4)_3HP_2O_7$ and $(NH_4)_4P_2O_7$, and the composition of the point is $\omega(CO(NH_2)_2 + NH_4NO_3)$ of

Table 1
The phase equilibria data of the ternary system (APP-[$CO(NH_2)_2$-NH_4NO_3]–H_2O) at 273.2 K and atmospheric pressure①

No.	Saturated liquid phase composition ω/% (mass)			Composition of plant nutrient in liquid phase ω/% (mass)			Equilibrium solid phase②
	$CO(NH_2)_2$ + NH_4NO_3	APP	H_2O	N	P_2O_5	N + P_2O_5	
1, E_1	0.00	56.49	43.51	10.70	33.78	44.47	T
2	7.39	53.01	39.59	13.01	31.70	44.70	T
3	10.62	48.28	41.10	13.40	28.86	42.27	T
4	14.18	45.16	40.66	14.24	27.00	41.24	T
5	18.77	39.85	41.36	15.08	23.83	38.91	T
6	24.03	32.31	43.64	15.77	19.32	35.09	T
7	27.53	31.23	41.22	16.97	18.67	35.64	T
8	28.47	28.94	42.58	16.91	17.30	34.21	T
9	31.18	27.03	41.77	17.64	16.16	33.80	T
10	32.71	25.80	41.48	18.02	15.42	33.44	T
11	33.70	24.83	41.45	18.23	14.85	33.08	T
12	37.54	19.43	43.01	18.75	11.62	30.36	T
13	39.72	20.60	26.97	19.84	12.32	32.16	T
14	42.87	15.03	42.08	20.06	8.99	29.04	T
15	47.63	13.30	39.05	21.64	7.95	29.59	T
16	53.02	10.54	36.42	23.28	6.30	29.58	T
17	53.73	7.47	31.31	22.98	4.46	27.45	T
18	54.38	8.30	37.29	23.41	4.96	28.37	T
19	58.41	5.78	30.01	24.54	3.45	28.00	T
20	59.41	5.63	34.93	24.92	3.37	28.29	T
21	61.62	5.72	32.63	25.82	3.42	29.24	T
22, C_1	64.73	4.73	30.51	26.88	2.83	29.71	T + P
23	66.90	1.90	31.16	27.22	1.14	28.36	P
24	69.30	1.36	29.31	28.08	0.81	28.89	P
25, F_1	81.53	0.21	18.23	32.77	0.12	32.90	P

① Standard uncertainties u are $u_c(CO(NH_2)_2 + NH_4NO_3) = 0.30\%$, $u_c(APP) = 0.69\%$ and $u(T) = 0.1$ K.
② T: $(NH_4)_3HP_2O_7$; P: $(NH_4)_4P_2O_7$.

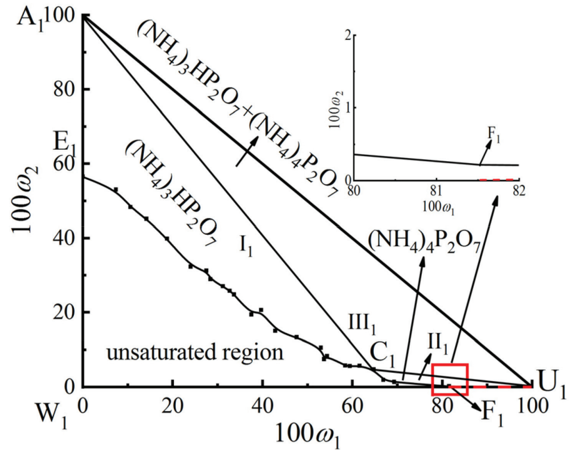

Fig. 3. Phase diagram for the ternary system APP-[$CO(NH_2)_2$-NH_4NO_3]–H_2O at 273.2 K. W_1, H_2O; U_1, $CO(NH_2)_2$ + NH_4NO_3; A_1, APP; E_1, solubility of APP in water; C_1, co-saturated point of $(NH_4)_3HP_2O_7$) and $(NH_4)_4P_2O_7$; F_1, solubility of APP in UAN solution; ω_1, mass fraction of $CO(NH_2)_2$ + NH_4NO_3; ω_2, mass fraction of APP.

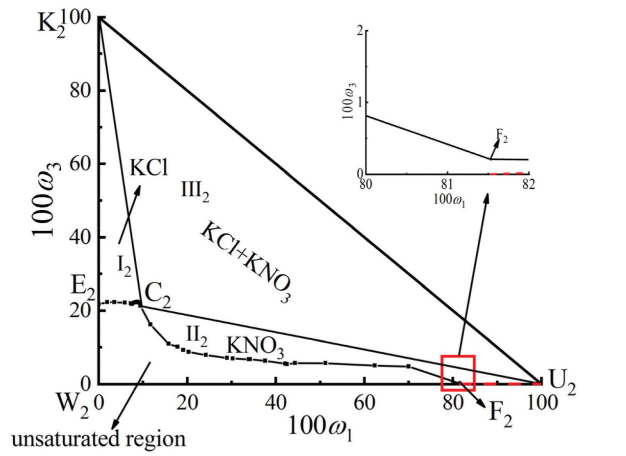

Fig. 4. Phase diagram for the ternary system KCl-[$CO(NH_2)_2$-NH_4NO_3]–H_2O at 273.2 K. W_2, H_2O; U_2, $CO(NH_2)_2$ + NH_4NO_3; K_2, KCl; E_2, solubility of KCl in water; C_2, co-saturated point of KCl and KNO_3; F_2, solubility of KCl in UAN solution; ω_1, mass fraction of $CO(NH_2)_2$ + NH_4NO_3; ω_3, mass fraction of KCl.

64.73% (mass) and ω(APP) of 4.73% (mass). The UAN solution contains not only $CO(NH_2)_2$ and NH_4NO_3, but also 18.25% (mass) H_2O. Point F_1 shows the solubility of APP in UAN solution because the UAN solution with 36.11% (mass) $CO(NH_2)_2$ and 45.60% (mass) NH_4NO_3 would not induce the crystallization at 273.2 K [17]. The composition of the point F_1 is ω($CO(NH_2)_2$ + NH_4NO_3) of 81.53% (mass) and ω(APP) of 0.21% (mass), and the maximum content of $CO(NH_2)_2$ and NH_4NO_3 in APP-[$CO(NH_2)_2$-NH_4NO_3]-H_2O system reached in this point. The illustration in Fig. 2 is a partial enlargement of point F_1. Because the limitation of the maximum salt content in UAN solution reaches 81.71%, the solubility data of $CO(NH_2)_2$ + NH_4NO_3 cannot be measured once larger than F_1 point. The red-dotted line was consequently used to represent the data from this point to U_1 point. Meanwhile, APP shows no salting-out effect neither on $CO(NH_2)_2$ nor NH_4NO_3.

3.2. Solid-liquid equilibrium of KCl-[$CO(NH_2)_2$-NH_4NO_3]–H_2O

According to the experimental results in Table 2, the phase diagram of ternary system KCl-[$CO(NH_2)_2$-NH_4NO_3]-H_2O at 273.2 K is shown in Fig. 4. The isothermal solubility diagram contains one invariant point C_2 and two solubility curves (E_2C_2 and C_2F_2,

Table 2
The phase equilibria data of the ternary system (KCl-[$CO(NH_2)_2$-NH_4NO_3]–H_2O) at 273.2 K and atmospheric pressure[①]

No.	Saturated liquid phase composition ω/% (mass)			Composition of plant nutrient in liquid phase ω/% (mass)			Equilibrium solid phase[②]
	$CO(NH_2)_2$ + NH_4NO_3	KCl	H_2O	N	K_2O	N + K_2O	
1, E_2	0.00	21.75	78.25	0.00	13.74	13.74	K
2	1.94	22.35	75.71	0.78	14.12	14.90	K
3	3.56	22.34	74.09	1.43	14.12	15.55	K
4	5.91	22.22	71.87	2.37	14.04	16.41	K
5	7.29	21.97	70.73	2.93	13.88	16.81	K
6	7.58	21.80	70.62	3.04	13.78	16.82	K
7	8.08	22.19	69.72	3.24	14.02	17.27	K
8	8.50	22.33	69.17	3.41	14.11	17.52	K
9	8.80	22.43	68.77	3.53	14.17	17.70	K
10	9.08	22.17	68.75	3.65	14.00	17.65	K
11, C_2	9.42	21.28	69.29	3.78	13.45	17.23	K + N
12	11.69	16.20	72.11	4.69	10.23	14.93	N
13	15.78	10.95	73.26	6.34	6.92	13.26	N
14	17.84	10.17	71.98	7.16	6.43	13.59	N
15	19.12	9.27	71.60	7.68	5.86	13.54	N
16	20.33	8.75	70.91	8.16	5.53	13.69	N
17	24.22	7.96	67.81	9.72	5.03	14.75	N
18	28.99	7.13	63.86	11.64	4.50	16.15	N
19	30.27	6.98	62.73	12.15	4.41	16.56	N
20	33.91	6.79	59.28	13.62	4.29	17.91	N
21	34.17	6.81	59.01	13.72	4.30	18.02	N
22	37.61	6.37	56.00	15.10	4.02	19.12	N
23	42.12	5.60	52.26	16.91	3.54	20.45	N
24	42.55	5.47	43.95	17.08	3.46	20.54	N
25	44.31	5.74	49.93	17.79	3.63	21.42	N
26	51.23	5.73	43.02	20.57	3.62	24.18	N
27	62.34	5.06	32.57	25.03	3.20	28.22	N
28	70.00	4.80	25.16	28.10	3.03	31.14	N
29, F_2	81.53	0.20	18.23	32.73	0.13	32.86	N

① Standard uncertainties u are u_c($CO(NH_2)_2$ + NH_4NO_3) = 0.30%, u_c(KCl) = 2.11% and $u(T)$ = 0.1 K.
② K: KCl; N: KNO_3.

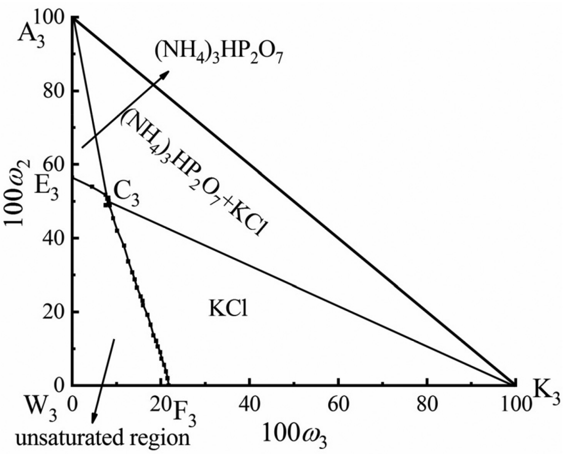

Fig. 5. Phase diagram for the ternary system APP-KCl-H_2O at 273.2 K. W_3, H_2O; K_3, KCl; A_3, APP; E_3, solubility of APP in water; C_3, co-saturated point of $(NH_4)_3HP_2O_7$ and KCl; F_3, solubility of KCl in water; ω_2, mass fraction of APP; ω_3, mass fraction of KCl.

corresponding to the crystallization of KCl and KNO_3, respectively). The invariant point C_2 is saturated with KCl and KNO_3, where the composition is $\omega(CO(NH_2)_2 + NH_4NO_3)$ of 9.42% (mass) and ω (KCl) of 21.28% (mass). The ternary system consists of two crystallization zones (I_2, II_2), one crystallization coexistence zone (III_2) as well. Point F_2 reflects the solubility of KCl in UAN solution. The composition of the point F_2 is $\omega(CO(NH_2)_2 + NH_4NO_3)$ of 81.53% (mass) and ω(KCl) of 0.20% (mass) and the maximum content of $CO(NH_2)_2$ and NH_4NO_3 in KCl-[$CO(NH_2)_2$-NH_4NO_3]-H_2O system reached in this point. The solubility above F_2 point (81.53% (mass)) in the phase equilibrium system is not measured due to the influence of water in UAN, hence, the red dotted line represents the solubility of phase equilibrium system ranging from F_2 to the vertex U_1. The metathesis reaction of KNO_3 is as Eq. (8), in which two compounds exchange components to form two other compounds.

$$KCl + NH_4NO_3 = KNO_3 + NH_4Cl \tag{8}$$

The substitution reaction occurs between KCl and NH_4NO_3 with the NH_4NO_3 increase in the UAN solution (Eq. (8)). In Fig. 4, the co-saturated region of KCl + KNO_3 is greater than single crystal region of KCl or KNO_3, while the areas of KCl and KNO_3 regions are similar. KCl and KNO_3 have no salting out effect on $CO(NH_2)_2$ in this system.

3.3. Solid-liquid equilibrium of APP-KCl-H_2O

Phase diagram of the APP-KCl-H_2O ternary system at 273.2 K is shown in Fig. 5. The corresponding solubility data are listed in Table 3. The isothermal solubility diagram contains one invariant point C_3, two solubility curves (E_3C_3 and C_3F_3, corresponding to the crystallization of $(NH_4)_3HP_2O_7$ and KCl, respectively), two crystallization zones ($A_3E_3C_3$, $C_3F_3K_3$) and one crystallization coexistence zone ($A_3C_3K_3$). The invariant point C_3 is saturated with $(NH_4)_3HP_2O_7$ and KCl, and the composition of the point is ω(KCl) of 7.96% (mass) and ω(APP) of 50.68% (mass). The crystal region of $(NH_4)_3HP_2O_7$ is much smaller than that of KCl. APP indicates a strong salting-out effect on KCl.

3.4. Solubility and phase diagram of quaternary system (APP-[$CO(NH_2)_2$-NH_4NO_3]-KCl-H_2O) at 273.2 K

The measured data of the APP-[$CO(NH_2)_2$-NH_4NO_3]-KCl-H_2O quaternary system at 273.2 K is listed in Table 4. The isothermal

Table 3
The phase equilibria data of the ternary system (APP-KCl-H_2O) at 273.2 K and atmospheric pressure[①]

No.	Saturated liquid phase composition ω/% (mass)			Composition of plant nutrient in liquid phase ω/% (mass)				Equilibrium solid phase[③]
	KCl	APP	H_2O	N	P_2O_5	K_2O	TPN[②]	
1, E_3	0.00	56.49	43.51	10.70	33.78	0.00	44.47	T
2	4.53	53.96	41.50	10.22	32.27	2.86	45.34	T
3	7.56	51.81	40.63	9.81	30.98	4.78	45.56	T
4	7.58	48.96	43.46	9.27	29.27	4.79	43.33	T
5, C_3	7.96	50.68	41.36	9.59	30.30	5.03	44.92	T + K
6	8.22	50.99	40.79	9.65	30.49	5.19	45.33	K
7	8.25	50.05	41.70	9.47	29.92	5.21	44.61	K
8	8.53	48.93	42.54	9.26	29.25	5.39	43.91	K
9	9.27	45.35	45.38	8.59	27.12	5.86	41.56	K
10	10.14	42.03	47.84	7.96	25.13	6.40	39.49	K
11	11.76	37.92	50.32	7.18	22.67	7.43	37.28	K
12	12.60	33.51	53.48	6.34	20.04	7.96	34.34	K
13	13.59	30.67	55.74	5.81	18.34	8.59	32.73	K
14	14.06	28.60	56.91	5.41	17.10	8.88	31.40	K
15	14.65	26.50	58.85	5.02	15.85	9.25	30.12	K
16	15.48	24.19	60.33	4.58	14.46	9.78	28.82	K
17	15.88	23.00	61.12	4.35	13.75	10.04	28.14	K
18	16.01	21.79	62.20	4.12	13.03	10.12	27.27	K
19	17.00	19.16	63.83	3.63	11.46	10.74	25.83	K
20	17.72	16.51	65.77	3.13	9.87	11.19	24.19	K
21	18.33	13.62	68.05	2.58	8.14	11.58	22.30	K
22	18.95	12.09	68.96	2.29	7.23	11.97	21.49	K
23	19.34	10.54	70.12	2.00	6.30	12.22	20.52	K
24	19.90	8.99	71.11	1.70	5.37	12.57	19.65	K
25	20.15	7.27	72.58	1.38	4.34	12.73	18.45	K
26	20.76	5.53	73.70	1.05	3.31	13.12	17.47	K
27	21.19	3.78	75.03	0.71	2.26	13.39	16.36	K
28	21.56	1.92	76.52	0.36	1.15	13.62	15.13	K
29, F_3	21.75	0.00	78.25	0.00	0.00	13.74	13.74	K

① Standard uncertainties u are u_c(APP) = 0.69%, u_c(KCl) = 2.11% and $u(T)$ = 0.1 K.
② TPN, total plant nutrient = N + P_2O_5 + K_2O.
③ T: $(NH_4)_3HP_2O_7$; K: KCl.

Table 4
Phase equilibrium data and density of the APP-[$CO(NH_2)_2$-NH_4NO_3]-KCl-H_2O system at 273.2 K and atmospheric pressure①

No.	Saturated liquid phase composition ω/% (mass)			H_2O/% (mass)	Composition of plant nutrient in liquid phase ω/% (mass)			TPN②/% (mass)	Composition of three forms nitrogen in liquid phase ω/% (mass)			ρ/g·cm^{-3}	Equilibrium solid phase③
	APP	$CO(NH_2)_2$ + NH_4NO_3	KCl		N	P_2O_5	K_2O		NH_4^+-N	NO_3^--N	$CO(NH_2)_2$-N		
1	4.42	7.23	20.40	67.95	3.74	2.64	12.89	19.27	1.54	0.71	1.49	1.19	K
2	9.47	7.56	19.11	63.86	4.83	5.66	12.07	22.56	2.53	0.74	1.56	1.19	K
3	8.06	6.49	19.63	65.82	4.13	4.82	12.40	21.35	2.16	0.64	1.34	1.20	K
4	5.05	4.11	14.49	76.34	3.57	4.13	12.52	20.22	1.86	0.55	1.16	1.20	K
5	12.70	6.69	18.05	62.56	5.09	7.59	11.40	24.08	3.05	0.65	1.38	1.24	K
6	11.06	5.87	18.83	64.23	4.45	6.62	11.90	22.97	2.67	0.57	1.21	1.23	K
7	9.79	5.22	19.13	65.86	3.95	5.85	12.09	21.89	2.36	0.51	1.08	1.22	K
8	45.35	0.00	9.27	45.38	8.59	27.12	5.86	41.56	8.59	0.00	0.00	1.37	K
9	42.03	0.00	10.14	47.84	7.96	25.13	6.40	39.49	7.96	0.00	0.00	1.35	K
10	37.92	0.00	11.76	50.32	7.18	22.67	7.43	37.28	7.18	0.00	0.00	1.33	K
11	33.65	0.00	12.65	53.70	6.37	20.12	7.99	34.48	6.37	0.00	0.00	1.31	K
12	28.72	0.00	14.12	57.16	5.44	17.17	8.92	31.53	5.44	0.00	0.00	1.29	K
13	23.00	0.00	15.88	61.12	4.35	13.75	10.04	28.14	4.35	0.00	0.00	1.26	K
14	16.51	0.00	17.72	65.77	3.13	9.87	11.19	24.19	3.13	0.00	0.00	1.23	K
15	8.99	0.00	19.90	71.11	1.70	5.37	12.57	19.65	1.70	0.00	0.00	1.19	K
16	50.05	0.00	8.25	41.70	9.47	29.92	5.21	44.61	9.47	0.00	0.00	1.39	K
17	13.98	0.00	2.44	12.16	9.26	29.25	5.39	43.91	9.26	0.00	0.00	1.39	K
18	30.67	0.00	13.59	13.83	5.81	18.34	8.59	32.73	5.81	0.00	0.00	1.30	K
19	12.69	0.00	7.01	28.18	5.02	15.85	9.25	30.12	5.02	0.00	0.00	1.28	K
20	24.19	0.00	15.48	60.33	4.58	14.46	9.78	28.82	4.58	0.00	0.00	1.27	K
21	21.79	0.00	16.01	62.20	4.12	13.03	10.12	27.27	4.12	0.00	0.00	1.26	K
22	4.15	0.00	3.68	13.83	3.63	11.46	10.74	25.83	3.63	0.00	0.00	1.25	K
23	13.62	0.00	18.33	68.05	2.58	8.14	11.58	22.30	2.58	0.00	0.00	1.22	K
24	12.09	0.00	18.95	68.96	2.29	7.23	11.97	21.49	2.29	0.00	0.00	1.21	K
25	10.54	0.00	19.34	70.12	2.00	6.30	12.22	20.52	2.00	0.00	0.00	1.20	K
26	7.84	0.00	21.73	78.27	1.38	4.34	12.73	18.45	1.38	0.00	0.00	1.31	K
27	1.15	0.00	4.31	15.29	1.05	3.31	13.12	17.47	1.05	0.00	0.00	1.18	K
28	3.78	0.00	21.19	75.03	0.71	2.26	13.39	16.36	0.71	0.00	0.00	1.17	K
29	1.92	0.00	21.56	76.52	0.36	1.15	13.62	15.13	0.36	0.00	0.00	1.16	K
30	8.25	5.33	19.65	66.76	3.70	4.94	12.41	21.05	2.08	0.52	1.10	1.21	K
31	3.15	8.13	20.84	67.88	3.86	1.88	13.17	18.91	1.39	0.80	1.68	1.20	K
32	12.56	5.71	18.38	63.34	4.67	7.51	11.61	23.80	2.93	0.56	1.18	1.23	K
33	12.39	5.29	18.26	64.06	4.47	7.41	11.53	23.41	2.86	0.52	1.09	1.24	K
34	3.13	6.84	20.72	69.30	3.34	1.87	13.09	18.30	1.26	0.67	1.41	1.19	K
35	3.31	8.69	20.51	67.49	4.11	1.98	12.95	19.05	1.47	0.85	1.79	1.20	K
36	2.47	8.48	20.89	68.16	3.87	1.48	13.20	18.55	1.29	0.83	1.75	1.20	K
37	1.68	9.25	20.91	68.15	4.03	1.00	13.21	18.25	1.22	0.90	1.91	1.20	K
38	1.43	5.83	21.21	71.53	2.61	0.85	13.40	16.86	0.84	0.57	1.20	1.18	K
39	1.64	7.96	21.01	69.39	3.51	0.98	13.27	17.76	1.09	0.78	1.64	1.19	K
40	1.44	2.73	21.32	74.51	1.37	0.86	13.47	15.70	0.54	0.27	0.56	1.17	K
41	1.35	5.56	21.46	71.63	2.49	0.80	13.56	16.85	0.80	0.54	1.15	1.18	K
42	1.29	1.40	21.46	75.85	0.81	0.77	13.56	15.13	0.38	0.14	0.29	1.16	K
43	0.87	0.44	21.61	77.08	0.34	0.52	13.65	14.52	0.21	0.04	0.09	1.16	K
44	3.27	3.46	21.02	72.26	2.01	1.95	13.28	17.24	0.96	0.34	0.71	1.18	K
45	39.63	1.34	10.33	48.70	8.04	23.69	6.53	38.26	7.63	0.13	0.28	1.34	K
46, C	0.00	0.00	21.75	78.25	0.00	0.00	13.74	13.74	0.00	0.00	0.00	1.15	K
47	0.00	9.08	22.17	68.75	3.65	0.00	14.00	17.65	0.88	0.89	1.87	1.19	K
48	0.00	8.80	22.43	68.77	3.53	0.00	14.17	17.70	0.86	0.86	1.82	1.18	K
49	0.00	8.50	22.33	69.17	3.41	0.00	14.11	17.52	0.83	0.83	1.75	1.18	K
50	0.00	8.08	22.19	69.72	3.24	0.00	14.02	17.27	0.79	0.79	1.67	1.18	K
51	0.00	7.58	21.80	70.62	3.04	0.00	13.78	16.82	0.74	0.74	1.56	1.18	K
52	0.00	7.29	21.97	70.73	2.93	0.00	13.88	16.81	0.71	0.71	1.50	1.18	K
53	0.00	5.91	22.22	71.87	2.37	0.00	14.04	16.41	0.58	0.58	1.22	1.17	K
54	0.00	3.56	22.34	74.09	1.43	0.00	14.12	15.55	0.35	0.35	0.73	1.16	K
55	0.00	1.94	22.35	75.71	0.78	0.00	14.12	14.90	0.19	0.19	0.40	1.16	K
56	5.30	8.62	20.03	66.05	4.46	3.17	12.65	20.28	1.84	0.84	1.78	1.20	K
57	7.82	6.22	13.28	72.67	5.68	6.68	11.19	23.54	2.98	0.87	1.83	1.20	K
58	14.96	7.76	17.50	59.78	5.95	8.94	11.05	25.95	3.59	0.76	1.60	1.25	K
59	48.96	0.00	7.58	43.46	9.27	29.27	4.79	43.33	9.27	0.00	0.00	1.38	K
60	10.48	3.79	11.46	74.27	5.33	9.53	11.00	25.85	3.58	0.56	1.19	1.25	K
61	17.38	5.34	16.90	60.38	5.43	10.39	10.68	26.50	3.81	0.52	1.10	1.26	K
62	22.38	5.08	15.61	56.93	6.28	13.38	9.86	29.52	4.73	0.50	1.05	1.28	K
63	27.19	5.66	15.24	51.90	7.10	15.56	9.21	31.87	5.45	0.53	1.12	1.30	K
64	29.59	5.52	13.51	51.37	7.82	17.69	8.54	34.05	6.14	0.54	1.14	1.32	K
65	18.24	3.22	7.30	71.24	8.23	18.91	8.00	35.14	6.53	0.55	1.15	1.32	K
66	43.13	3.36	9.66	43.85	9.51	25.79	6.10	41.41	8.49	0.33	0.69	1.37	K
67	11.34	18.54	7.91	62.20	9.59	6.78	5.00	21.37	3.95	1.81	3.83	1.20	N
68	8.45	13.69	11.29	66.56	7.10	5.05	7.13	19.28	2.93	1.34	2.82	1.19	N
69	6.40	10.32	17.74	65.54	5.36	3.83	11.21	20.39	2.22	1.01	2.13	1.19	N
70, J	0.00	15.78	10.95	73.26	6.34	0.00	6.92	13.26	1.54	1.54	3.25	1.13	N
71	0.00	20.33	8.75	70.91	8.16	0.00	5.53	13.69	1.98	1.99	4.19	1.13	N

(*continued on next page*)

Table 4 (*continued*)

No.	Saturated liquid phase composition ω/% (mass)			H_2O/% (mass)	Composition of plant nutrient in liquid phase ω/% (mass)			TPN②/% (mass)	Composition of three forms nitrogen in liquid phase ω/% (mass)			ρ/g·cm^{-3}	Equilibrium solid phase③
	APP	$CO(NH_2)_2$ + NH_4NO_3	KCl		N	P_2O_5	K_2O		NH_4^+-N	NO_3^--N	$CO(NH_2)_2$-N		
72	0.00	11.69	16.20	72.11	4.69	0.00	10.23	14.93	1.14	1.14	2.41	1.15	N
73	32.74	14.54	5.15	47.56	12.04	19.58	3.25	34.87	7.61	1.42	3.00	1.32	N
74	23.47	17.03	6.31	53.19	11.28	14.03	3.99	29.30	6.10	1.67	3.51	1.27	N
75	15.69	12.10	11.34	60.87	7.83	9.38	7.16	24.37	4.15	1.18	2.50	1.23	N
76	8.28	27.27	6.69	57.75	12.52	4.95	4.23	21.69	4.22	2.67	5.63	1.21	N
77	20.96	10.40	11.08	57.56	8.14	12.53	7.00	27.68	4.98	1.02	2.15	1.26	N
78	0.00	28.99	7.13	63.86	11.64	0.00	4.50	16.15	2.82	2.84	5.98	1.16	N
79	0.00	17.84	10.17	71.98	7.16	0.00	6.43	13.59	1.74	1.75	3.68	1.13	N
80	5.56	19.55	8.82	66.07	8.90	3.32	5.57	17.80	2.96	1.91	4.03	1.17	N
81	5.05	16.84	10.05	68.05	7.72	3.02	6.35	17.09	2.60	1.65	3.47	1.16	N
82	4.39	14.69	11.63	69.28	6.73	2.63	7.35	16.70	2.26	1.44	3.03	1.16	N
83	15.45	24.22	5.90	54.42	12.65	9.24	3.73	25.61	5.28	2.37	5.00	1.23	N
84	9.45	15.43	10.48	64.63	7.98	5.65	6.62	20.25	3.29	1.51	3.18	1.19	N
85	7.19	11.72	14.81	66.27	6.07	4.30	9.36	19.73	2.50	1.15	2.42	1.19	N
86	23.24	22.88	5.15	48.72	13.24	13.54	3.17	29.96	6.46	2.18	4.60	1.27	N
87	17.68	18.04	7.02	57.25	10.59	10.57	4.44	25.60	5.10	1.76	3.72	1.23	N
88	14.61	15.20	8.71	61.48	8.87	8.74	5.50	23.10	4.25	1.49	3.14	1.21	N
89	7.61	8.08	10.23	74.07	6.53	6.34	9.01	21.88	3.11	1.10	2.32	1.21	N
90	19.17	14.37	8.43	58.02	9.40	11.46	5.32	26.19	5.03	1.41	2.96	1.24	N
91	12.14	12.82	11.69	63.35	7.44	7.26	7.38	22.08	3.55	1.25	2.64	1.21	N
92	13.36	10.46	13.93	62.25	6.73	7.99	8.80	23.52	3.55	1.02	2.16	1.22	N
93	0.00	24.22	7.96	67.81	9.72	0.00	5.03	14.75	2.36	2.37	5.00	1.15	N
94	0.00	19.12	9.27	71.60	7.68	0.00	5.86	13.54	1.86	1.87	3.95	1.14	N
95	4.66	23.86	7.65	63.82	10.46	2.78	4.83	18.08	3.20	2.33	4.92	1.18	N
96	3.23	16.64	10.53	69.59	7.29	1.93	6.65	15.87	2.23	1.63	3.43	1.16	N
97	2.68	13.87	6.87	76.58	8.35	2.20	5.97	16.52	2.55	1.86	3.93	1.16	N
98	5.63	59.41	0.00	56.00	15.10	0.00	4.02	19.12	3.66	3.68	7.76	1.19	N
99	9.17	22.74	7.20	60.88	10.87	5.48	4.55	20.90	3.95	2.22	4.69	1.20	N
100	7.27	18.37	9.02	60.88	8.75	4.34	5.70	18.79	3.16	1.80	3.79	1.18	N
101	5.61	14.15	8.12	72.12	8.06	4.01	6.13	18.21	2.92	1.65	3.49	1.18	N
102	6.09	15.39	10.62	67.89	7.33	3.64	6.71	17.69	2.65	1.51	3.18	1.17	N
103	17.82	27.28	5.23	49.66	14.33	10.66	3.30	28.28	6.03	2.67	5.63	1.26	N
104	13.07	21.05	6.91	58.97	10.92	7.81	4.36	23.10	4.52	2.06	4.34	1.21	N
105	9.94	16.28	9.54	64.22	8.42	5.94	6.03	20.39	3.47	1.59	3.36	1.19	N
106	9.03	14.77	10.52	65.68	7.64	5.40	6.64	19.68	3.15	1.44	3.05	1.19	N
107	18.46	21.20	5.85	54.47	12.01	11.04	3.70	26.74	5.56	2.07	4.37	1.24	N
108	4.02	27.40	7.19	61.39	11.76	2.40	4.54	18.70	3.43	2.68	5.65	1.18	N
109	3.22	22.26	8.35	66.17	9.54	1.92	5.28	16.74	2.78	2.18	4.59	1.16	N
110	2.89	19.99	8.90	68.21	8.57	1.73	5.62	15.92	2.49	1.96	4.12	1.15	N
111	2.60	36.82	6.10	54.46	15.27	1.56	3.86	20.69	4.08	3.60	7.59	1.20	N
112	6.37	21.54	7.94	64.14	9.85	3.81	5.02	18.68	3.30	2.11	4.44	1.18	N
113	9.94	21.75	7.34	60.96	10.61	5.95	4.64	21.20	4.00	2.13	4.49	1.20	N
114	8.58	19.04	8.35	64.02	9.27	5.13	5.28	19.67	3.48	1.86	3.93	1.19	N
115	11.73	25.23	6.38	56.65	12.35	7.01	4.03	23.39	4.68	2.47	5.20	1.22	N
116	12.47	20.17	7.41	59.94	10.46	7.46	4.68	22.60	4.32	1.97	4.16	1.21	N
117	19.09	23.23	5.58	52.09	12.94	11.41	3.53	27.88	5.88	2.27	4.79	1.25	N
118	15.40	19.46	7.26	57.86	10.73	9.21	4.59	24.53	4.81	1.90	4.01	1.22	N
119	13.99	17.80	7.99	60.22	9.79	8.36	5.05	23.20	4.38	1.74	3.67	1.22	N
120	3.71	31.38	6.49	58.40	13.30	2.22	4.10	19.62	3.76	3.07	6.47	1.19	N
121	2.92	25.15	7.63	64.29	10.65	1.75	4.82	17.22	3.00	2.46	5.19	1.17	N
122	2.59	22.40	8.21	66.79	9.48	1.55	5.19	16.22	2.67	2.19	4.62	1.16	N
123	2.23	19.43	9.14	69.19	8.22	1.33	5.78	15.33	2.31	1.90	4.01	1.15	N
124	14.28	26.35	7.34	52.02	12.03	7.73	4.20	23.96	4.77	2.33	4.92	1.22	N
125	10.59	22.64	8.69	58.07	10.30	5.88	5.10	21.27	3.91	2.06	4.33	1.20	N
126	9.85	20.48	8.71	60.96	9.50	5.55	5.18	20.23	3.64	1.89	3.98	1.19	N
127	5.35	18.89	9.94	65.81	8.32	3.10	6.08	17.49	2.76	1.79	3.77	1.17	N
128	26.20	30.46	4.86	58.66	14.77	13.47	2.64	30.88	6.81	2.56	5.40	1.28	N
129	48.53	9.21	12.03	30.22	9.86	22.21	5.82	37.90	7.72	0.69	1.45	1.34	N
130	59.38	13.12	6.41	21.08	12.11	26.04	2.97	41.12	9.18	0.94	1.98	1.36	N
131	43.59	15.18	7.17	34.06	11.24	20.43	3.55	35.23	7.63	1.16	2.45	1.31	N
132	50.69	12.97	7.37	28.97	11.21	22.94	3.52	37.67	8.22	0.96	2.03	1.33	N
133	27.09	19.48	9.69	43.73	11.05	13.82	5.22	30.09	5.99	1.63	3.43	1.27	N
134	46.65	16.28	6.39	30.67	11.85	21.52	3.12	36.49	8.04	1.23	2.59	1.32	N
135	38.90	7.44	7.49	46.16	10.35	23.26	4.73	38.34	8.09	0.73	1.54	1.34	N
136	34.51	10.69	6.41	48.38	10.83	20.63	4.05	35.51	7.57	1.05	2.21	1.31	N
137	30.69	9.60	8.45	51.26	9.66	18.35	5.34	33.35	6.74	0.94	1.98	1.30	N
138	26.23	10.66	8.78	54.32	9.25	15.69	5.55	30.48	6.00	1.04	2.20	1.27	N
139	20.70	10.62	11.19	57.48	8.18	12.38	7.07	27.63	4.95	1.04	2.19	1.25	N
140	14.79	12.29	11.34	61.58	7.73	8.84	7.16	23.74	4.00	1.20	2.53	1.22	N
141	8.00	12.07	13.25	66.67	6.36	4.79	8.37	19.52	2.69	1.18	2.49	1.20	N
142	28.25	17.79	4.73	49.22	12.49	16.89	2.99	32.37	7.08	1.74	3.67	1.29	N

(*continued on next page*)

Table 4 (*continued*)

No.	Saturated liquid phase composition ω/% (mass)			H_2O/% (mass)	Composition of plant nutrient in liquid phase ω/% (mass)			TPN②/% (mass)	Composition of three forms nitrogen in liquid phase ω/% (mass)			ρ/g·cm^{-3}	Equilibrium solid phase③
	APP	$CO(NH_2)_2$ + NH_4NO_3	KCl		N	P_2O_5	K_2O		NH_4^+-N	NO_3^--N	$CO(NH_2)_2$-N		
143	23.17	20.72	5.17	50.93	12.70	13.85	3.27	29.82	6.40	2.03	4.27	1.27	N
144	18.76	20.61	6.12	54.49	11.83	11.22	3.87	26.91	5.56	2.02	4.25	1.25	N
145	13.17	22.49	6.93	57.06	11.56	7.90	4.39	23.86	4.70	2.21	4.65	1.22	N
146	6.93	25.30	7.18	60.58	11.47	4.14	4.53	20.15	3.78	2.48	5.22	1.19	N
147	7.77	10.53	17.14	64.55	5.70	4.65	10.83	21.17	2.50	1.03	2.17	1.21	N
148	6.69	12.89	12.68	67.72	6.44	4.00	8.01	18.46	2.52	1.26	2.66	1.18	N
149	5.01	13.41	12.11	69.47	6.33	2.99	7.65	16.97	2.25	1.31	2.77	1.18	N
150	3.47	14.30	12.20	70.02	6.40	2.07	7.71	16.18	2.05	1.40	2.95	1.16	N
151	3.25	39.43	5.55	51.75	16.45	1.94	3.51	21.90	4.46	3.86	8.13	1.22	N
152	3.59	13.71	11.75	70.95	6.18	2.14	7.42	15.75	2.01	1.34	2.83	1.15	N
153	3.25	10.93	16.51	69.31	5.00	1.94	10.43	17.38	1.68	1.07	2.25	1.18	N
154	8.52	15.40	9.96	66.11	7.80	5.09	6.29	19.18	3.11	1.51	3.18	1.18	N
155	8.59	16.63	8.85	65.92	8.30	5.14	5.59	19.03	3.25	1.63	3.43	1.18	N
156	8.75	18.01	8.31	64.92	8.89	5.23	5.25	19.37	3.41	1.76	3.72	1.18	N
157	8.38	21.35	7.26	62.99	10.16	5.01	4.59	19.76	3.67	2.09	4.40	1.19	N
158	9.53	24.27	6.74	59.46	11.55	5.70	4.26	21.50	4.17	2.37	5.01	1.20	N
159	3.41	15.53	10.75	70.30	6.88	2.04	6.79	15.71	2.16	1.52	3.20	1.16	N
160	2.65	13.99	11.85	71.51	6.12	1.58	7.48	15.19	1.86	1.37	2.89	1.15	N
161	2.69	12.97	13.05	71.28	5.72	1.61	8.24	15.57	1.77	1.27	2.68	1.16	N
162	2.34	10.31	18.44	68.91	4.58	1.40	11.65	17.63	1.45	1.01	2.13	1.19	N
163	2.19	11.55	15.08	71.18	5.05	1.31	9.52	15.88	1.54	1.13	2.38	1.16	N
164	1.64	7.96	21.01	57.21	8.47	13.01	6.44	27.92	5.17	1.06	2.24	1.26	N
165	1.44	2.73	21.32	59.71	7.94	10.32	7.20	25.46	4.40	1.14	2.40	1.24	N
166, F	0.00	70.00	4.80	25.16	28.10	0.00	3.03	31.14	6.82	6.85	14.44	1.32	N
167	0.00	42.12	5.60	52.26	16.91	0.00	3.54	20.45	4.10	4.12	8.69	1.21	N
168	0.00	44.31	5.74	49.93	17.79	0.00	3.63	21.42	4.31	4.33	9.14	1.22	N
169	0.00	34.17	6.81	59.01	13.72	0.00	4.30	18.02	3.33	3.34	7.05	1.18	N
170	0.00	42.55	5.47	43.95	17.08	0.00	3.46	20.54	4.14	4.16	8.78	1.21	N
171	0.00	33.91	6.79	59.28	13.62	0.00	4.29	17.91	3.30	3.32	7.00	1.18	N
172	0.00	30.27	6.98	62.73	12.15	0.00	4.41	16.56	2.95	2.96	6.24	1.17	N
173	24.73	20.51	5.68	49.07	12.92	14.79	3.59	31.29	6.68	2.01	4.23	1.28	N
174	29.00	16.24	4.96	49.80	12.01	17.34	3.13	32.48	7.07	1.59	3.35	1.29	N
175	32.06	12.99	5.59	49.36	11.28	19.17	3.53	33.98	7.33	1.27	2.68	1.30	N
176	6.69	33.07	5.95	54.27	14.54	4.00	3.76	22.31	4.49	3.24	6.82	1.28	N
177	12.49	29.86	5.32	52.32	14.35	7.47	3.36	25.18	5.27	2.92	6.16	1.24	N
178	5.61	37.03	5.22	52.12	15.93	3.35	3.30	22.58	4.67	3.62	7.64	1.22	N
179	5.12	41.75	5.29	47.82	17.73	3.06	3.34	24.13	5.03	4.08	8.61	1.23	N
180	2.62	46.23	5.23	45.90	19.06	1.57	3.30	23.92	5.00	4.52	9.54	1.24	N
181	11.38	40.40	4.47	43.73	18.38	6.80	2.82	28.00	6.09	3.95	8.33	1.27	N
182	0.00	62.34	5.06	32.57	25.03	0.00	3.20	28.22	6.07	6.10	12.86	1.29	N
183	0.00	51.23	5.73	43.02	20.57	0.00	3.62	24.18	4.99	5.01	10.57	1.24	N
184, B	0.00	81.53	0.20	18.23	32.73	0.00	0.13	32.86	7.94	7.98	16.82	1.34	N
185	32.31	24.03	0.00	43.64	15.77	19.32	0.00	35.09	8.46	2.35	4.96	1.30	T
186	89.15	4.79	0.00	6.06	12.15	34.07	0.00	46.22	11.21	0.30	0.64	1.39	T
187	73.33	6.40	9.23	10.75	11.27	30.03	4.00	45.30	9.94	0.43	0.90	1.40	T
188	79.75	11.12	0.00	9.12	13.01	31.70	0.00	44.70	10.76	0.72	1.53	1.37	T
189	49.82	8.09	0.44	41.65	12.68	29.79	0.28	42.74	10.22	0.79	1.67	1.38	T
190	38.67	15.71	3.69	41.92	13.63	23.12	2.33	39.08	8.85	1.54	3.24	1.34	T
191	84.28	8.29	2.10	5.33	12.57	32.76	0.87	46.20	10.93	0.53	1.11	1.40	T
192	38.02	25.96	0.00	36.01	17.62	22.73	0.00	40.35	9.73	2.54	5.35	1.37	T
193	13.30	47.63	0.00	39.05	21.64	7.95	0.00	29.59	7.15	4.66	9.82	1.27	T
194	5.78	58.41	0.00	35.79	24.54	3.45	0.00	28.00	6.78	5.71	12.05	1.27	T
195	5.63	59.41	0.00	34.93	24.92	3.37	0.00	28.29	6.85	5.81	12.26	1.28	T
196	8.30	54.38	0.00	37.29	23.41	4.96	0.00	28.37	6.87	5.32	11.22	1.27	T
197	7.47	53.73	0.00	38.78	22.98	4.46	0.00	27.45	6.65	5.26	11.08	1.26	T
198	15.03	42.87	0.00	42.08	20.06	8.99	0.00	29.04	7.02	4.19	8.84	1.27	T
199	11.28	56.75	0.00	31.95	23.28	6.30	0.00	29.58	7.16	5.19	10.94	1.28	T
200	23.59	45.49	0.00	30.89	19.84	12.32	0.00	32.16	7.77	3.89	8.19	1.29	T
201	56.49	0.00	0.00	43.51	10.70	33.78	0.00	44.47	10.70	0.00	0.00	1.37	T
202	5.72	61.62	0.00	32.63	25.82	3.42	0.00	29.24	7.08	6.03	12.71	1.28	T
203	1.91	71.15	0.50	26.40	28.93	1.14	0.31	30.39	7.29	6.96	14.68	1.31	T
204	1.01	32.54	2.25	64.18	26.40	1.20	2.84	30.44	6.69	6.34	13.37	1.31	T
205	24.83	33.70	0.00	41.45	18.23	14.85	0.00	33.08	7.98	3.30	6.95	1.28	T
206	19.43	37.54	0.00	43.01	18.75	11.62	0.00	30.36	7.33	3.67	7.74	1.28	T
207	8.27	54.56	1.46	35.69	23.47	4.94	0.92	29.33	6.88	5.34	11.25	1.28	T
208	9.30	54.10	1.59	34.99	23.48	5.56	1.00	30.04	7.03	5.29	11.16	1.28	T
209	15.77	43.54	0.94	39.73	20.47	9.43	0.59	30.49	7.23	4.26	8.98	1.28	T
210	15.61	42.64	1.04	40.68	20.08	9.34	0.66	30.07	7.11	4.17	8.80	1.28	T
211	24.70	31.67	1.35	42.27	17.39	14.77	0.85	33.01	7.76	3.10	6.53	1.30	T
212	29.26	28.06	0.90	41.77	16.80	17.49	0.57	34.87	8.27	2.75	5.79	1.31	T
213	35.68	21.36	0.56	42.39	15.33	21.33	0.35	37.02	8.84	2.09	4.41	1.32	T

(*continued on next page*)

Table 4 (*continued*)

No.	Saturated liquid phase composition ω/% (mass)			H_2O/% (mass)	Composition of plant nutrient in liquid phase ω/% (mass)			TPN②/% (mass)	Composition of three forms nitrogen in liquid phase ω/% (mass)			ρ/g·cm^{-3}	Equilibrium solid phase③
	APP	$CO(NH_2)_2$ + NH_4NO_3	KCl		N	P_2O_5	K_2O		NH_4^+-N	NO_3^--N	$CO(NH_2)_2$-N		
214	36.85	19.07	0.97	43.09	14.63	22.03	0.61	37.28	8.83	1.87	3.93	1.33	T
215, D	60.04	0.04	0.00	39.92	11.13	35.10	0.00	46.23	11.37	0.00	0.01	1.41	T
216	53.96	0.00	4.53	41.50	10.22	32.27	2.86	45.34	10.22	0.00	0.00	1.38	T
217	50.99	0.00	8.22	40.79	9.65	30.49	5.19	45.33	9.65	0.00	0.00	1.39	T
218	41.90	0.00	6.11	51.98	9.81	30.98	4.78	45.56	9.81	0.00	0.00	1.39	T
219	25.80	32.71	0.00	41.48	18.02	15.42	0.00	33.44	8.07	3.20	6.75	1.29	T
220	27.03	31.18	0.00	41.77	17.64	16.16	0.00	33.80	8.15	3.05	6.43	1.30	T
221	28.94	28.47	0.00	42.58	16.91	17.30	0.00	34.21	8.25	2.78	5.87	1.30	T
222	31.23	27.53	0.00	41.36	16.97	18.67	0.00	35.64	8.59	2.69	5.68	1.30	T
223	39.85	18.77	0.00	41.22	15.08	23.83	0.00	38.91	9.37	1.84	3.87	1.33	T
224	45.16	14.18	0.00	40.66	14.24	27.00	0.00	41.24	9.93	1.39	2.92	1.34	T
225	48.28	10.62	0.00	41.10	13.40	28.86	0.00	42.27	10.17	1.04	2.19	1.35	T
226	1.90	66.90	0.00	31.16	27.22	1.14	0.00	28.36	6.87	6.54	13.80	1.28	P
227	1.36	69.30	0.00	29.31	28.08	0.81	0.00	28.89	7.00	6.78	14.30	1.40	P
228	2.59	65.86	1.66	29.85	26.93	1.55	1.05	29.53	6.90	6.44	13.59	1.30	P
229	1.71	67.72	3.55	26.98	27.51	1.02	2.25	30.78	6.92	6.63	13.97	1.32	P
230	1.77	65.72	4.38	28.10	26.72	1.06	2.77	30.55	6.73	6.43	13.56	1.31	P
231	0.21	81.53	0.00	18.23	32.77	0.12	0.00	32.90	7.98	7.98	16.82	1.34	P
232	8.92	9.55	18.29	63.24	5.52	5.33	11.55	22.41	2.62	0.93	1.97	1.22	K + N
233	26.95	7.47	12.23	53.34	8.10	16.11	7.73	31.94	5.83	0.73	1.54	1.29	K + N
234, H	8.34	1.70	1.98	11.49	9.62	21.21	5.31	36.14	7.42	0.71	1.49	1.33	K + N
235, I	0.00	9.42	21.28	69.29	3.78	0.00	13.45	17.23	0.92	0.92	1.94	1.19	K + N
236	12.48	36.92	5.79	44.78	15.75	6.84	3.35	25.94	5.46	3.31	6.98	1.24	T + N
237	29.56	20.43	4.14	45.86	13.80	17.67	2.62	34.09	7.59	2.00	4.21	1.30	T + N
238	22.86	25.28	4.26	47.59	14.48	13.67	2.69	30.84	6.79	2.47	5.21	1.28	T + N
239	16.69	30.94	4.72	47.63	15.58	9.98	2.98	28.55	6.17	3.03	6.38	1.26	T + N
240	19.39	29.24	4.42	46.93	15.41	11.59	2.79	29.80	6.52	2.86	6.03	1.27	T + N
241	23.87	27.68	3.98	44.46	15.63	14.27	2.52	32.42	7.21	2.71	5.71	1.29	T + N
242	9.86	4.71	1.14	12.30	13.42	21.04	2.58	37.03	8.30	1.65	3.47	1.32	T + N
243	32.11	17.11	4.38	46.40	12.95	19.20	2.76	34.91	7.74	1.67	3.53	1.31	T + N
244	2.16	54.98	4.50	38.34	22.48	1.29	2.84	26.61	5.76	5.38	11.34	1.27	T + N
245	6.47	49.03	5.09	39.39	20.91	3.87	3.21	27.99	6.00	4.80	10.11	1.28	T + N
246	7.28	47.59	4.97	40.14	20.48	4.35	3.14	27.98	6.01	4.66	9.82	1.27	T + N
247	8.89	46.71	5.02	39.36	20.44	5.32	3.17	28.92	6.23	4.57	9.63	1.28	T + N
248	11.34	43.83	4.59	40.23	19.74	6.78	2.90	29.42	6.41	4.29	9.04	1.29	T + N
249	12.20	38.75	5.08	51.96	17.87	7.30	3.21	28.37	6.08	3.79	7.99	1.27	T + N
250	4.05	10.21	1.33	12.33	17.42	8.67	3.02	29.11	6.31	3.58	7.54	1.27	T + N
251	17.86	34.25	4.48	43.40	17.13	10.68	2.83	30.64	6.72	3.35	7.07	1.29	T + N
252	20.13	30.07	4.62	45.17	15.88	12.04	2.92	30.84	6.74	2.94	6.20	1.28	T + N
253	21.78	23.90	4.92	49.39	13.72	13.02	3.11	29.85	6.45	2.34	4.93	1.27	T + N
254, E	4.73	64.73	0.00	30.51	26.88	2.83	0.00	29.71	7.20	6.33	13.35	1.28	T + P
255	3.27	66.18	2.09	28.43	27.19	1.96	1.32	30.46	7.06	6.47	13.65	1.31	T + P
256	2.98	67.13	2.80	27.06	27.52	1.78	1.77	31.07	7.10	6.57	13.85	1.31	T + P
257, G	50.68	0.00	7.96	41.36	9.59	30.30	5.03	44.92	9.59	0.00	0.00	1.39	T + K

① Standard uncertainties u are u_c(APP) = 0.69%, u_c($CO(NH_2)_2$ + NH_4NO_3) = 0.30%, u_c(KCl) = 2.11%, u_c(N) = 0.35%, u_c(P_2O_5) = 0.67%, u_c(K_2O) = 2.08%, u_c(NH_4^+ − N) = 0.42%, u_c(NO_3^- − N) = 0.48%, u_c($CO(NH_2)_2$-N) = 0.48%, $u(\rho)$ = 0.0002 g·cm^{-3} and $u(T)$ = 0.1 K.
② TPN, total plant nutrient = N + P_2O_5 + K_2O.
③ K, KCl; N, KNO_3; T, $(NH_4)_3HP_2O_7$; P, $(NH_4)_4P_2O_7$.

solubility phase diagram was plotted in Fig. 6. As shown in Fig. 6, the solubility was described as N-P_2O_5-K_2O system so as to facilitate liquid fertilizer (*e.g.*, APP, UAN and KCl) used in agriculture. The solid lines show the contours of constant TPN in the diagram. For example, contour line labeled 18.72 represents that the TPN along the line is equal to 18.72 at 273.2 K. The broken lines are connected by points with the same co-saturated salt in adjacent crystalline regions, and the corresponding crystallizing phase is divided into four regions. Points A, B(ω(N) = 32.73% (mass), ω(P_2O_5) = 0.00% (mass), ω(K_2O) = 0.13% (mass)), C(ω(N) = 0.00% (mass), ω(P_2O_5) = 0.00% (mass), ω(K_2O) = 13.74% (mass)) represent plant nutrient of P_2O_5, N, K_2O, respectively. The TPN reaches the maximum and minimum at point D (ω(N) = 11.13% (mass), ω(P_2O_5) = 35.10% (mass), ω(K_2O) = 0.00% (mass)), and J(ω(N) = 6.34% (mass), ω(P_2O_5) = 0.00% (mass), ω(K_2O) = 6.92% (mass)) with values of 46.23% (mass) and 13.26% (mass), respectively. The isothermal solubility diagram consists of three phase boundaries (EF, GF, GHI) and four zones (DEFG, EBF, GFIH, and GHIC, corresponding to $(NH_4)_3HP_2O_7$, $(NH_4)_4P_2O_7$, KNO_3, and KCl crystallization, respectively). The contents of each component in the subsystem systems of APP-[$CO(NH_2)_2$-NH_4NO_3]–H_2O, KCl-[$CO(NH_2)_2$-NH_4NO_3]-H_2O and APP-KCl-H_2O were converted into N, P_2O_5 and K_2O contents, which can be represented as curves DB, BC and DC in Fig. 6, respectively. The curve AC shows that the sub-system contains only P_2O_5, but there is no component that contains P only in the raw material. Hence that field ADC is an invalid zone where solution fertilizer formulation can impossibly proceed. Since curve BC is the ternary KCl-[$CO(NH_2)_2$-NH_4NO_3]–H_2O system without the crystallization of $(NH_4)_3HP_2O_7$ or $(NH_4)_4P_2O_7$, the roughly estimated point F (ω(K_2O) = 28.10% (mass), ω(P_2O_5) = 0.00% (mass), ω(N) = 3.03% (mass)) acts as the endpoint of curve GF.

With respect to the diverse crystallizations generated in the phase diagram of the quaternary systems APP-[$CO(NH_2)_2$-NH_4NO_3]-KCl-H_2O and APP(11-37-0)-[$CO(NH_2)_2$-NH_4NO_3]-KCl-H_2O(TVA) [11] at 273.2 K, there were five crystallization regions

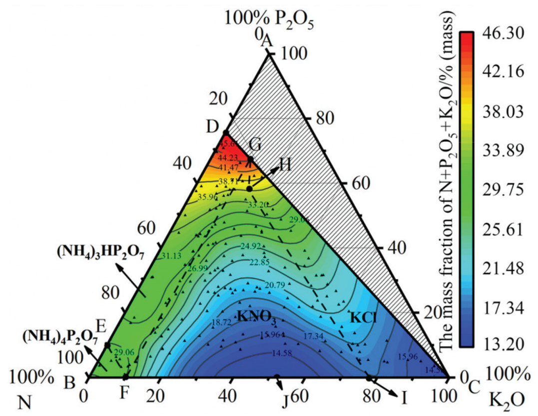

Fig. 6. Three-component solubility phase diagram for the quaternary system APP-[$CO(NH_2)_2$-NH_4NO_3]-KCl-H_2O at 273.2 K. A, P_2O_5; B, N; C, K_2O; D, the point of maximum TPN; E, co-saturated point of $(NH_4)_3HP_2O_7$ and $(NH_4)_4P_2O_7$; F, the crystallization point of KNO_3; G, co-saturated point of $(NH_4)_3HP_2O_7$ and KCl; H and I, co-saturated point of KNO_3 and KCl; J, the point of minimum TPN.

($(NH_4)_5P_3O_{10}{\cdot}2H_2O$, NH_4Cl, NH_4NO_3, KNO_3 and KCl) for the later system, but no crystallization of NH_4Cl and NH_4NO_3 while emerging the crystal of $(NH_4)_4P_2O_7$ for the former system studied within our work. The crystallization region of $(NH_4)_3HP_2O_7$ and $(NH_4)_4P_2O_7$ in the left side (AB) of Fig. 6 is larger than the corresponding crystallization area of $(NH_4)_5P_3O_{10}{\cdot}2H_2O$ in the phase diagram of APP(11-37-0)-UAN-KCl-H_2O. The potential reason is that the content of NH_4^+-N in solid APP(18-58-0) is higher than the one of NH_4^+-N in liquid APP(11-37-0), which results in a more significant ion effect. Finally, all the polyphosphate is easier to salt out in the APP(18-58-0)-[$CO(NH_2)_2$-NH_4NO_3]-KCl-H_2O system than the APP (11-37-0)-UAN-KCl-H_2O system. Another interesting finding is the crystallization zone of $(NH_4)_4P_2O_7$ is located at the lower left corner (B) in Fig. 6, which could be attributed to the phosphorous species of the studied APP which contains orthophosphate and pyrophosphate only. The pyrophosphate is composed of $(NH_4)_3HP_2O_7$ and $(NH_4)_4P_2O_7$ (Fig. 1(b)). The pH value increases with enhanced NH_4^+, and the reaction moves to the right direction of Eq. (9). More $(NH_4)_4P_2O_7$ is generated in EBF region subsequently.

$$(NH_4)_2HPO_4 + (NH_4)_3HP_2O_7 = (NH_4)_4P_2O_7 + (NH_4)H_2PO_4 \quad (9)$$

The XRD patterns shown in Fig. 7(a), (b), (c) and (d) well coincide with the four co-saturated regions of KNO_3 + KCl, $(NH_4)_3HP_2O_7$ + KCl, $(NH_4)_3HP_2O_7$ + KNO_3, and $(NH_4)_3HP_2O_7$ + $(NH_4)_4P_2O_7$, respectively.

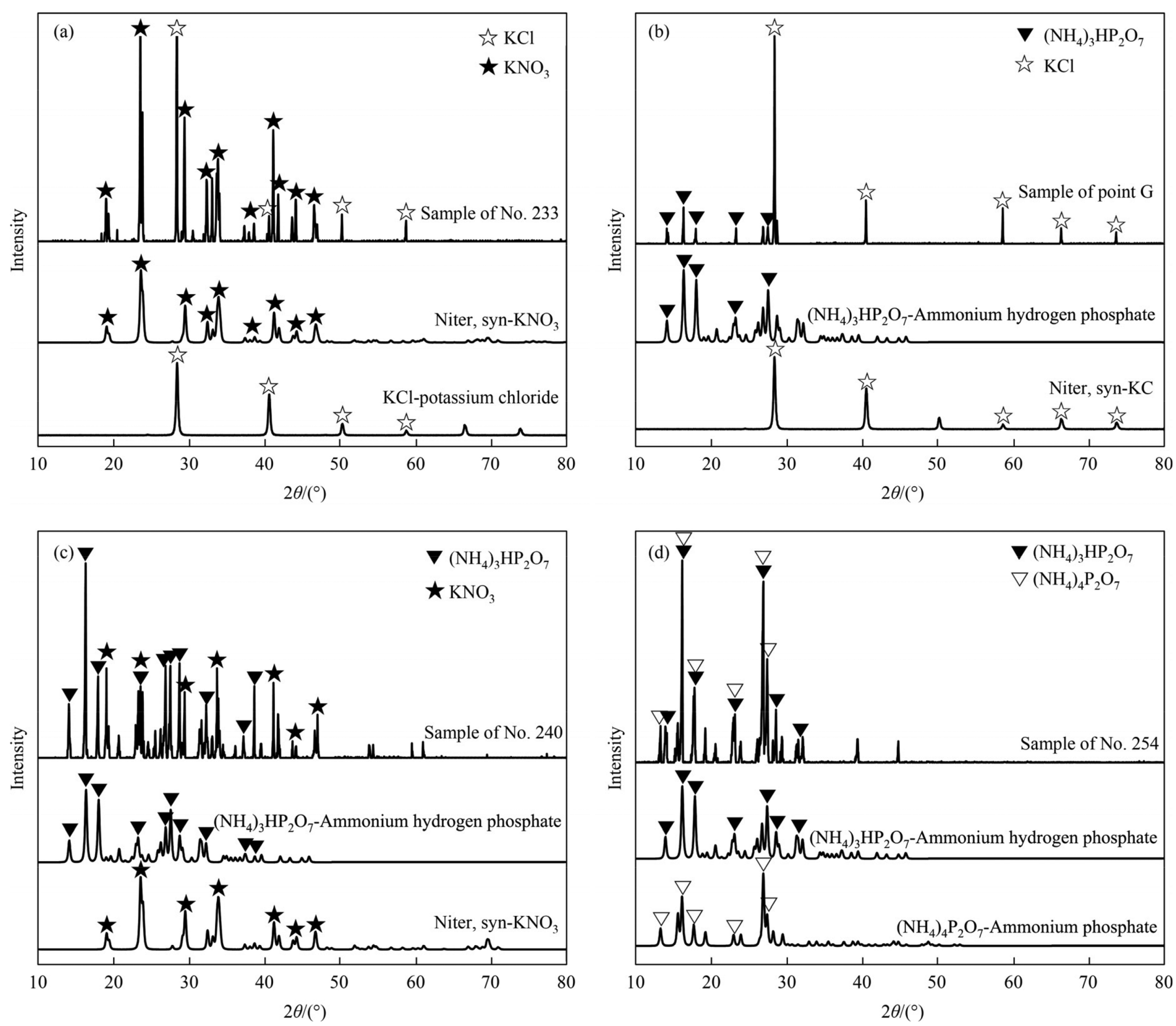

Fig. 7. X-ray diffraction pattern of invariant point KNO_3 + KCl (a), $(NH_4)_3HP_2O_7$ + KCl (b), $(NH_4)_3HP_2O_7$ + KNO_3 (c) and $(NH_4)_3HP_2O_7$ + $(NH_4)_4P_2O_7$ (d) of the quaternary system APP-[$CO(NH_2)_2$-NH_4NO_3]-KCl-H_2O at 273.2 K.

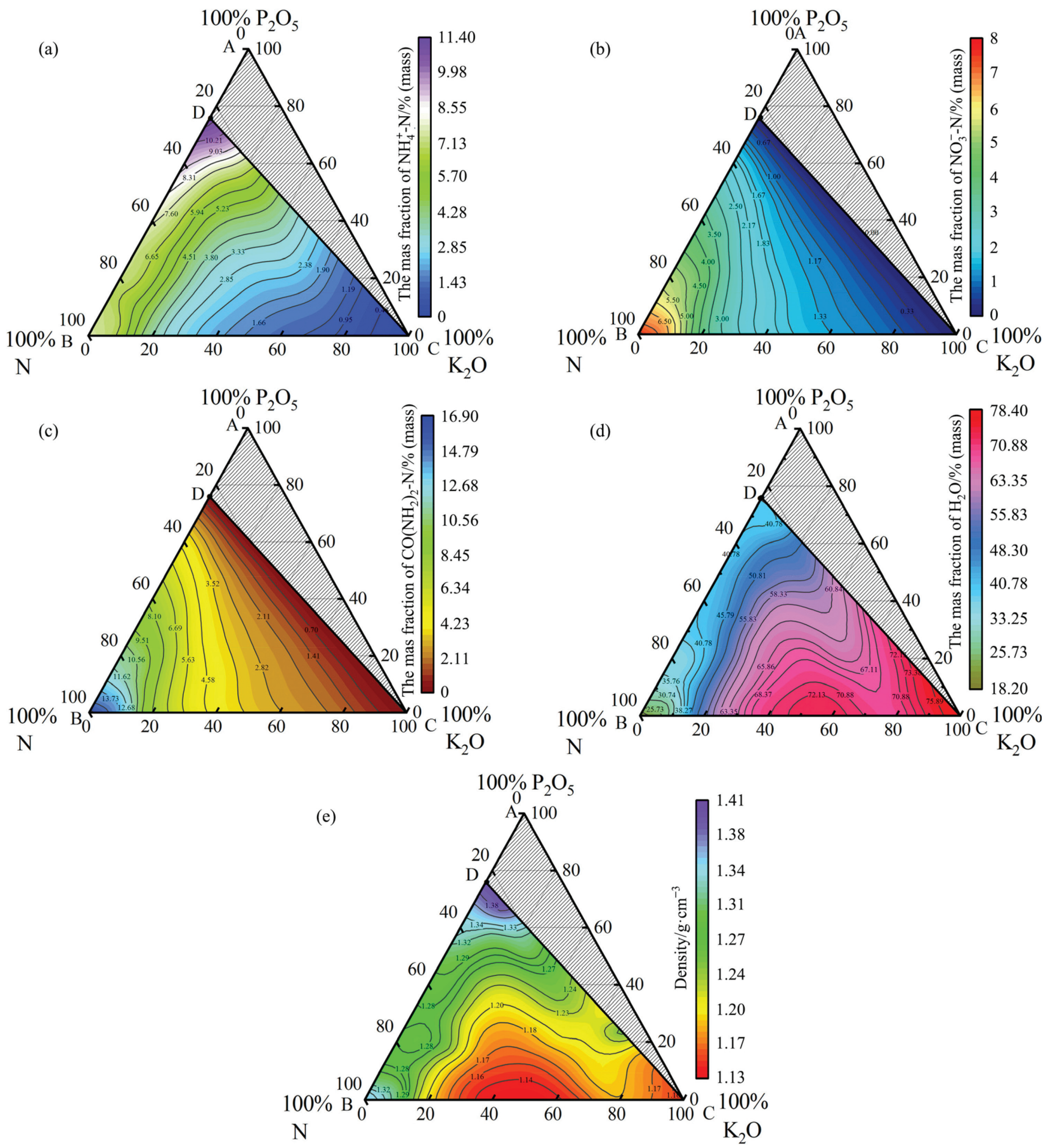

Fig. 8. The mass fraction of NH_4^+-N (a), NO_3^--N (b), $CO(NH_2)_2$-N (c), H_2O (d) and density (e) of the three-component solubility diagram APP-[$CO(NH_2)_2$-NH_4NO_3]-KCl-H_2O at 273.2 K.

3.5. Three forms of nitrogen ($NH_4^+ - N$, $NO_3^- - N$ and $CO(NH_2)_2$-N), water content and density of APP-[$CO(NH_2)_2$-NH_4NO_3]-KCl-H_2O system at 273.2 K

The TPN content is easily accessible through the phase diagram of Fig. 6, however, different crops show up variational demands for NH_4^+-N, NO_3^--N, and $CO(NH_2)_2$-N. These formulas are also important to facilitate the nutritional requirements in different growing periods. The diagram of nitrogen content of NH_4^+-N, NO_3^--N, $CO(NH_2)_2$-N, water content and density with the solubility of the APP-[$CO(NH_2)_2$-NH_4NO_3]-KCl-H_2O system was drawn in Fig. 8(a)–(e), basing the data in Table 4. In Fig. 8(a)–(e), the solid lines reveal the contours of constant NH_4^+-N, NO_3^--N, $CO(NH_2)_2$-N, water content and density, respectively. As shown in Fig. 8(a), (d) and (e), the content of NH_4^+-N and solution density increases gradually corresponding to the increase of TPN content (Fig. 6), and finally, reaches up to the maximum at point D, while the water content decreases with increased TPN. The reason might be that a large proportion of NH_4^+-N is provided by APP, of which the trend is basically the same as that of TPN content. In Fig. 8(b) and (c), the NO_3^--N and $CO(NH_2)_2$-N increases with elevated total nitrogen, reaching its maximum at point B. The potential reason is that UAN is the source of NO_3^--N/$CO(NH_2)_2$-N, the overall trend of NO_3^--N and $CO(NH_2)_2$-N content is just in accordance with total nitrogen (NH_4^+-N + NO_3^--N + $CO(NH_2)_2$-N) content.

4. Conclusions

In this work, the solid–liquid phase equilibrium of quaternary system APP-[$CO(NH_2)_2$-NH_4NO_3]-KCl-H_2O and its three subsystems (APP-[$CO(NH_2)_2$-NH_4NO_3]-H_2O, KCl-[$CO(NH_2)_2$-NH_4NO_3]-H_2O and APP-KCl-H_2O) at the temperature of 273.2 K were studied by a dynamic method. The ternary systems of APP-[$CO(NH_2)_2$-NH_4NO_3]-H_2O, KCl-[$CO(NH_2)_2$-NH_4NO_3]-H_2O and APP-KCl-H_2O contain two single crystal regions (($(NH_4)_3HP_2O_7$ and $(NH_4)_4P_2O_7$; KCl and KNO_3; $(NH_4)_3HP_2O_7$ and KCl, respectively) and one co-saturated crystal region (($(NH_4)_3HP_2O_7$ + $(NH_4)_4P_2O_7$; KCl + KNO_3; $(NH_4)_3HP_2O_7$ + KCl, respectively). The first two ternary systems have no salting-out effect on $CO(NH_2)_2$, while in APP-KCl-H_2O system, APP shows a strong salting-out effect on KCl. The phase diagram of quaternary system APP-[$CO(NH_2)_2$-NH_4NO_3]-KCl-H_2O is consisted of four solid phase crystallization regions (($(NH_4)_3HP_2O_7$, $(NH_4)_4P_2O_7$, KNO_3 and KCl), but no quaternary invariant points. The maximum TPN content existing as ionic forms in the ternary and quaternary systems is 32.86%–45.56% (mass) and 46.23% (mass), respectively, indicating that the maximum nutrient content can be reached using raw materials from the corresponding systems to prepare liquid fertilizer. In the quaternary system, the content of NH_4^+-N increases gradually corresponding to the increase of TPN content and the NO_3^--N and $CO(NH_2)_2$-N increases with elevated total N. The phase-equilibrium data obtained in this study provides a theoretical basis for the preparation of liquid fertilizers with different N: P_2O_5: K_2O ratios, especially for a formula involving solid polyphosphates as feedstock.

Data Availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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