Solid-liquid phase equilibrium of ammonium dihydrogen phosphate and agricultural grade ammonium polyphosphate (Degree of polymerization ranged from 1 to 8) for mixed irrigation strategy

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**Uncertainty assessment methods**

The uncertainties of all reported quantities in manuscript are assessed with reference to the following method. The relative standard uncertainty, \( u_r(x) \), was calculated as follows:

\[
u_r(x) = \frac{u}{x}\]

Where \( u \) and \( x \) were standard uncertainty and the average of experimental data, respectively. In order to calculate the \( U \), the standard deviation (\( S \)) and the instrumental error (\( \Delta \)) were needed.

\[
u = \sqrt{S^2 + \Delta^2}\]

\( S \) can be expressed with the experiment times (\( n \)), the experimental data (\( x_i \)) and \( x \).

\[
S = \sqrt{\frac{\sum(x_i - x)^2}{n - 1}}
\]

Therefore, on the basis of series experimental data, \( u_r(x) \) of different quantities can be calculated to evaluate the uncertainty.
Comparison analysis between experimental results and available literature data

Table S1. Comparison of MAP solubility data in literature and experiment in water: Literature 1# Ref. ¹, Literature 2# Ref. ², Literature 3#, 4#, 5#, 6# Ref. ³.

| T / K | Experimental | Lit. 1# | Lit. 2# | Lit. 3# | Lit. 4# | Lit. 5# | Lit. 6# |
|-------|--------------|---------|---------|---------|---------|---------|---------|
| 278.2 | 0.0371       | none    | none    | none    | none    | none    | none    |
| 283.2 | 0.0419       | 0.0425  | 0.0411  | none    | none    | none    | none    |
| 288.2 | 0.0470       | none    | none    | none    | none    | none    | none    |
| 293.2 | 0.0527       | 0.0528  | 0.0533  | none    | none    | none    | none    |
| 298.2 | 0.0587       | none    | none    | none    | none    | none    | none    |
| 303.3 | 0.0645       | 0.0644  | 0.0633  | none    | none    | none    | none    |
| 308.2 | 0.0719       | none    | none    | none    | none    | none    | none    |
| 313.2 | 0.0800       | 0.0808  | 0.0806  | 0.0821  | 0.0819  | 0.0812  | 0.0803  |
| 323.2 | none         | 0.0937  | 0.0976  | none    | none    | none    | none    |
| 333.2 | none         | 0.1130  | 0.1153  | none    | none    | none    | none    |

Figure S1. Comparison of literature and experimental data: (a) Solubility of MAP in water: Literature 1# Ref. ¹, Copyright 2016 American Chemical Society, Literature 2# Ref. ², Copyright 1920 Elsevier, Literature 3#, 4#, 5#, 6# Ref. ³, Copyright 2017 Elsevier; (b) Density of MAP solution: Literature 1# Ref. ⁴, Copyright 1984 American Chemical Society, Literature 2# Ref. ⁵, Copyright 2017 American Chemical Society, Literature 3# Ref. ⁶, Copyright 2019 American Chemical Society, Literature 4# Ref. ⁷, Copyright 2021 Elsevier, Literature 5# Ref. ³, Copyright 2017 Elsevier.

Table S2. Comparison of the MAP solution density data in literature and experiment: Literature 1# Ref. ⁴, Copyright 1984 American Chemical Society, Literature 2# Ref. ⁵, Copyright 2017 American Chemical Society, Literature 3# Ref. ⁶, Copyright 2019 American Chemical Society, Literature 4# Ref. ⁷, Copyright 2021 Elsevier, Literature 5# Ref. ³, Copyright 2017 Elsevier.

| T/K  | Molality (mol/kg) | Experimental ρ (g/cm³) | T/K  | Molality (mol/kg) | Lit. 1# ρ (g/cm³) | Lit. 2# ρ (g/cm³) | Lit. 3# ρ (g/cm³) | Lit. 4# ρ (g/cm³) |
|------|------------------|------------------------|------|------------------|-------------------|-------------------|-------------------|-------------------|
| 278.2| 2.140            | 1.120                  |      |                  | 0.500             | 1.030             | 1.030             | 1.030             |
| 283.2| 2.430            | 1.130                  | 288.2| 1.500            | 1.082             | 1.082             | 1.083             | 1.082             |
| 288.2| 2.740            | 1.140                  |      |                  | 2.000             | 1.105             | 1.106             | none              |
| 293.2| 3.090            | 1.150                  |      |                  | 3.470             | 1.160             | 1.054             | 1.054             |
| 298.2| 3.470            | 1.160                  | 298.2| 5.000            | 1.027             | 1.027             | 1.026             | 1.027             |
| 303.2| 3.830            | 1.180                  |      |                  | 1.000             | 1.054             | 1.054             | 1.054             |
| 308.2| 4.310            | 1.190                  |      |                  | 1.500             | 1.079             | 1.079             | 1.080             |
| 313.2| 4.830            | 1.200                  |      |                  | 2.000             | 1.102             | 1.102             | none              |

S3
| T/K  | Molality (mol/kg) | Lit. 5# | ρ (g/cm³) |
|------|------------------|--------|----------|
| 308.2|                  |        |          |
| 0.500| 1.023            | 1.024  | 1.023    | 1.024    |
| 1.000| 1.050            | 1.051  | 1.051    | 1.051    |
| 1.500| 1.075            | 1.076  | 1.076    | 1.076    |
| 2.000| 1.098            | 1.099  | none     | 1.099    |
| 313.2| 4.968            | 1.2044 |          |
| 318.2|                  |        |          |
| 0.500| 1.020            | 1.020  | 1.020    | 1.020    |
| 1.000| 1.046            | 1.047  | 1.046    | 1.047    |
| 1.500| 1.071            | 1.072  | 1.072    | 1.072    |
| 2.000| 1.094            | 1.095  | none     | 1.095    |
Research practical significance introduction

APP1 and MAP were both good phosphate fertilizer materials and had their own product advantages. The development of their hybrid formulation was a potential advantage strategy that not only provided both fast-release and slow-release phosphorus but also improved solubility to save irrigation water. Therefore, this study systematically explored the phase equilibrium law of APP-MAP-water ternary system, hoping to provide guidance for practical application of fertilizer. Considering the actual use cost and demand, this paper focused on the change rule of the system property when a small amount of APP1 was mixed with a large amount of MAP to achieve dissolution equilibrium. We had found that the combination of the two can facilitate dissolution and thus increase nutrient content in the same amount of solvent water. And we calculated the following proportion parameters to evaluate the change of phosphorus content in the mixed system. After adding APP1, the total P$_2$O$_5$ content in the solution system when MAP dissolution reached equilibrium was calculated as follows

$$P_2O_{5\;\text{Total}\%} = \frac{m_1 \cdot P_2O_{5\;\text{APP}\%} + m_2 \cdot P_2O_{5\;\text{MAP}\%}}{m_0 + m_1 + m_2} \times 100\%$$

And the ratio of P$_2$O$_5$ content in APP1 and MAP to total P$_2$O$_5$ in the system were calculated as follows

$$P_2O_{5\;\text{APP}\%} = \frac{m_1 \cdot P_2O_{5\;\text{APP}\%}}{m_1 \cdot P_2O_{5\;\text{APP}\%} + m_2 \cdot P_2O_{5\;\text{MAP}\%}} \times 100\%$$

$$P_2O_{5\;\text{MAP}\%} = \frac{m_2 \cdot P_2O_{5\;\text{MAP}\%}}{m_1 \cdot P_2O_{5\;\text{APP}\%} + m_2 \cdot P_2O_{5\;\text{MAP}\%}} \times 100\%$$

where, $m_0$, $m_1$ and $m_2$ represents the mass of water, APP1 and MAP, g; $P_2O_{5\;\text{APP}\%}$ is the content of P$_2$O$_5$ in watersoluble APP per unit mass, %; $P_2O_{5\;\text{MAP}\%}$ is the content of P$_2$O$_5$ per unit mass MAP, %.

Within the research scope, the phosphorus content of the same amount of MAP saturated solutions with or without APP1 were compared, and the maximum content of P$_2$O$_5$ provided by APP1 at different temperatures was shown in Table S3. The amount of APP1 was the maximum amount (0.8860 mol/kgH$_2$O) within the research range.

| T / K | P$_2$O$_5$MAP % (Purw water) | P$_2$O$_5$APP1 % (Mixing) | P$_2$O$_5$Total % (Mixing) |
|-------|-----------------------------|---------------------------|--------------------------|
| 278.2 | 12.20                       | 41.07                     | 23.07                    |
| 283.2 | 13.46                       | 38.82                     | 23.89                    |
| 288.2 | 14.78                       | 36.87                     | 24.65                    |
| 293.2 | 16.17                       | 42.06                     | 25.52                    |
| 298.2 | 17.58                       | 33.11                     | 26.26                    |
| 303.2 | 18.86                       | 31.26                     | 27.13                    |
| 308.2 | 20.44                       | 29.40                     | 28.06                    |
| 313.2 | 22.05                       | 27.71                     | 28.97                    |

*a Phosphorus content in MAP saturated aqueous solution.

*b Phosphorus content provided by APP1 in the ternary equilibrium system under maximum APP1 addition.

*c Phosphorus content of ternary equilibrium system under maximum APP1 addition.

It can be seen from Table S3 that the mixture of APP1 and MAP can significantly improve the nutrient content of the system compared with the single use of MAP, and the added slow-release phosphorus source also had the potential to improve the phosphorus utilization rate. Therefore, they can be synergistically co-dissolved and used under the specific environment and fertilizer demand to achieve economic efficiency. This study also opened up ideas and built a certain data foundation for expanding the application scheme of new phosphate fertilizer products.
Real-time online particle analysis technology

The real-time online particle analysis technology is mainly composed of the Focused Beam Reflectance Measurement (FBRM), which can track and record the change of particle size and particle quantity in real time, and the Particle-View Measurement (PVM), which can continuously observe the specific change of particle and particle structure. FBRM is a quantitative measurement tool that can be used to directly measure particle size, shape and quantity, and the resulting online data can be used to help understand and optimize dynamic processes. Therefore, this technology is used to observe the process of particle dissolution in water, and determine whether the solution is complete by analyzing the change of particle size. When FBRM can hardly detect the presence of particles, it indicates that the particles are completely dissolved in the liquid phase. The probe structure and optical measurement principle of FBRM are shown in Figure S2.

Figure S2. Probe structure and optical measurement principle of FBRM

Figure S3. The chord length of particles is measured by FBRM in the system

When the window comes into contact with particulate matter in the fluid system, it will monitor the pulsed reflected and scattered light and record the measured chord length, as shown in Figure S3. Due to the limitations of FBRM probe structure and principle,
FBRM can only detect the change of chord length of particles, but can not get the data of particle size. There are obvious differences in the shape and scanning Angle of particles in the system, and the obtained chord length data is not completely equivalent to the particle size results, but it can still directly reflect the change of particle size and shape. Therefore, we use this online particle analysis system to judge whether the dissolution process is complete, in our experiment after adding the APP1 particles only 1.6 particles with a size smaller than 10 microns and 0.4 particles with a size in the range of 10 to 50 microns existed, so we judge the system of particles is almost completely dissolved and verify the MAP and the APP has mutual promoting effect when mixed solution. The actual experiment is shown in Figure S4.

Figure S4. Application of on-line monitoring system in practical experiment. The images in Figure S4 were taken by Xiaohou Zhou, one of the authors.

Reference

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