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# Solubility Polytherm of the Ternary System Hexamethylenetetramine–Ammonium Dihydrogen Phosphate–Water

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**Abstract** — The solubility polytherm of the ternary system hexamethylenetetramine–ammonium dihydrogen phosphate–water was studied in a wide temperature range. The concentration and temperature ranges of crystallization of the starting components and a new compound, $NH_4H_2PO_4 \cdot 2(CH_2)_6N_4 \cdot 8H_2O$, were determined. The properties and structure of the new compound were studied by X-ray phase, thermal, and IR spectroscopic analyses.

Hexamethylenetetramine $(CH_2)_6N_2$ and ammonium dihydrogen phosphate $NH_4H_2PO_4$ are nitrogen and phosphorus fertilizers. To reveal interactions between $(CH_2)_6N_4$ and $NH_4H_2PO_4$ and to determine the composition and properties of a new compound formed by them, we studied the solubility polytherm of the ternary system $(CH_2)_6N_4$–$NH_4H_2PO_4$–$H_2O$.

The solubility polytherm of the system $(CH_2)_6N_4$–$NH_4H_2PO_4$–$H_2O$ was studied with 14 internal sections, of which sections I–VIII were drawn from the $H_2O$–$NH_4H_2PO_4$ side to the $(CH_2)_6N_4$ vertex, and sections IX–XIV, from the $H_2O$–$(CH_2)_6N_4$ side to the $NH_4H_2PO_4$ vertex.

From the results obtained with sections I–VIII and IX–XIV, and also from our data on the binary systems $H_2O$–$(CH_2)_6N_4$ and $H_2O$–$NH_4H_2PO_4$ (data on these systems are also given in [1, 2], we constructed the solubility diagram of the ternary system $(CH_2)_6N_4$–$NH_4H_2PO_4$–$H_2O$ (Fig. 1). The polytherm contains the crystallization fields of the starting compounds [ice, ammonium dihydrogen phosphate, hexamethylenetetramine (hexahydrate and anhydrous)] and of a new solid phase identified by chemical analysis as $NH_4H_2PO_4 \cdot 2(CH_2)_6N_4 \cdot 8H_2O$. Found, %: C 26.80; H 8.68; N 23.57. $C_{12}H_{46}N_{13}O_{12}P$. Calculated, %: C 26.71; H 8.53; N 23.37.

The compositions of the nodes of the system $(CH_2)_6N_4$–$NH_4H_2PO_4$–$H_2O$ and the corresponding temperatures are given in the table.

The major part of the diagram is occupied by the crystallization fields of hexamethylenetetramine, ammonium dihydrogen phosphate, and ice, and the minor part, by those of the new solid phases forming in the system, including hexamethylenetetramine hexahydrate.

The isotherms demonstrating the curvature of the corresponding sections of the diagram are plotted at 10°C intervals.

The X-ray diffraction patterns of $(CH_2)_6N_4$, ammonium dihydrogen phosphate, and a new compound (Fig. 2) are essentially different. The X-ray diffraction pattern of the synthesized compound contains no reflections belonging to the starting compounds, suggesting its purity.

The heating curve of $NH_4H_2PO_4 \cdot 2(CH_2)_6N_4 \cdot 8H_2O$ contains an endoeffect at 222°C with 43.4% weight loss, suggesting decomposition of the compound. This effect is followed in the DTA curve by exoeffects at 408, 545, and 630°C. Surprisingly, in the range 270–540°C, there is weight gain rather than weight loss. Apparently, in this temperature range, $(CH_2)_6N_4$ in the presence of ammonium dihydrogen phosphate transforms into new compounds. It is known that, at 195–250°C, the main decomposition products of $(CH_2)_6N_4$ are ammonia and a heterocyclic amine $(C_2H_3N)_x$ as an oily residue.

Above 300°C, hydrogen cyanide, methane, hydrogen, and nitrogen are released. In the range 600–800°C, the tarry oily residue transforms into a solid containing 74% C [3, 4].

Apparently, ammonium dihydrogen phosphate affects the thermolysis of $(CH_2)_6N_4$. We found that $NH_4H_2PO_4 \cdot 2(CH_2)_6N_4 \cdot 8H_2O$ above 600°C fully decomposes as a result of exothermic processes and gets carbonized.

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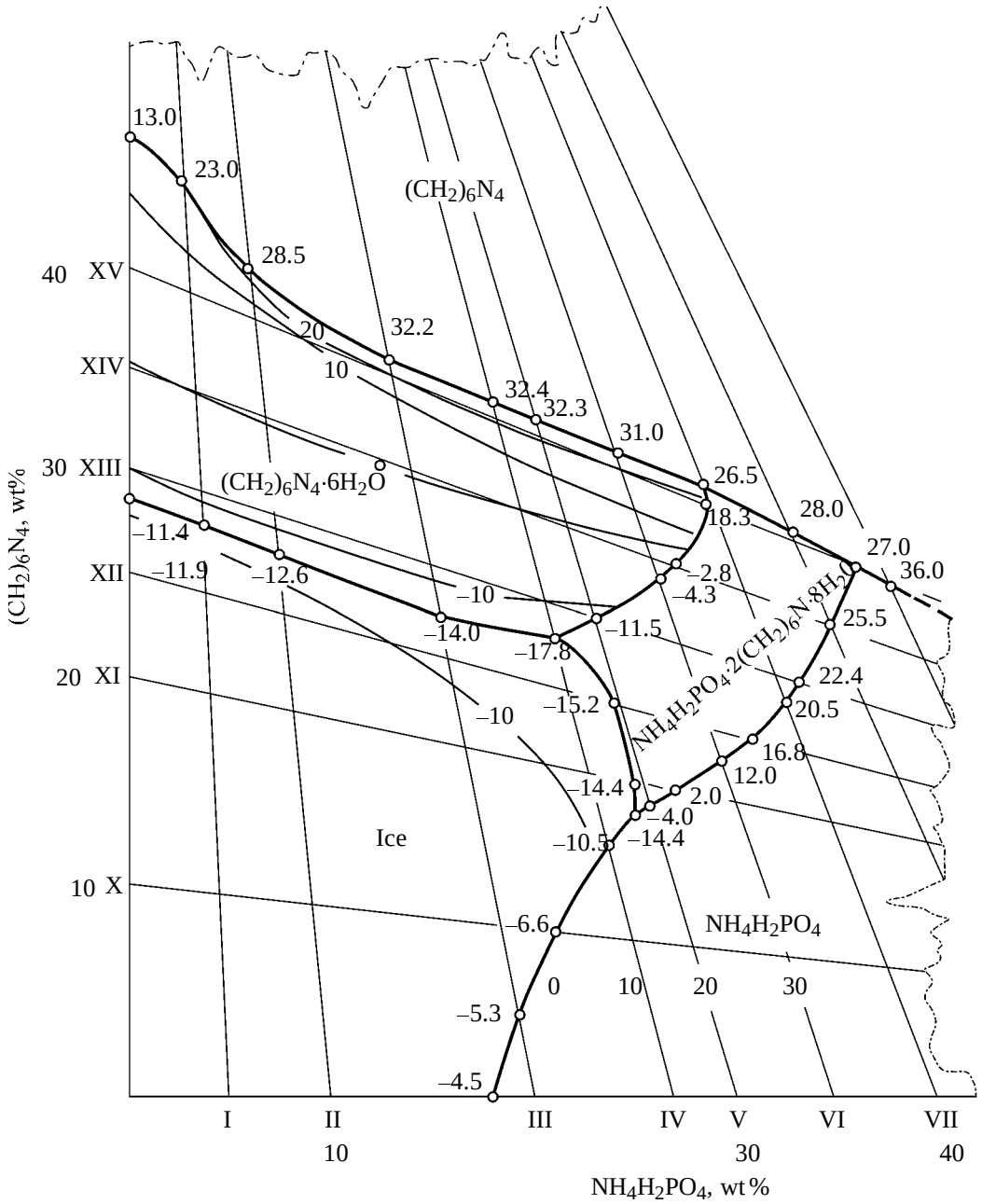


**Fig. 1.** Solubility polytherm of the ternary system hexamethylenetetramine–ammonium dihydrogen phosphate–water.

The IR spectrum of $NH_4H_2PO_4 \cdot 2(CH_2)_6N_4 \cdot 8H_2O$ contains absorption bands at 555, 960, 1130, 1300, and 1415 $cm^{-1}$. Comparison of the IR spectrum of $NH_4H_2PO_4 \cdot 2(CH_2)_6N_4 \cdot 8H_2O$ with that of $(CH_2)_6N_4$ shows that the absorption bands at 675, 825, 1240, and 2800 $cm^{-1}$ are split in two or three bands in the spectrum of the new compound, especially those of C–H stretching vibrations. These changes may be due to acid–base interaction of $(CH_2)_6N_4$ with $NH_4H_2PO_4$, and also to changes in the symmetry of $(CH_2)_6N_4$.

Thus, our study of the ternary system $(CH_2)_6N_4$–$NH_4H_2PO_4$–$H_2O$ revealed formation of a new compound, $NH_4H_2PO_4 \cdot 2(CH_2)_6N_4 \cdot 8H_2O$; its composition and purity were determined by elemental, X-ray phase, thermal, and IR spectroscopic analyses. The

Formation of crystalline phases in the system $(CH_2)_6N_4$–$NH_4H_2PO_4$–$H_2O$

| Composition, wt % | | | Crystallization temperature, °C | Equilibrium solid phases |
|---|---|---|---|---|
| $(CH_2)_6N_4$ | $NH_4H_2PO_4$ | $H_2O$ | | |
| 4.0 | 19.2 | 76.8 | –5.3 | Ice + $NH_4H_2PO_4$ |
| 7.7 | 21.2 | 71.1 | –6.6 | Ice + $NH_4H_2PO_4$ |
| 12.0 | 23.8 | 64.2 | –10.5 | Ice + $NH_4H_2PO_4$ |
| 13.5 | 25.0 | 61.5 | –14.4 | Ice + $NH_4H_2PO_4 \cdot 2(CH_2)_6N_4 \cdot 8H_2O$ + $NH_4H_2PO_4$ |
| 15.0 | 24.5 | 60.5 | –14.4 | Ice + $NH_4H_2PO_4 \cdot 2(CH_2)_6N_4 \cdot 8H_2O$ |
| 19.0 | 24.0 | 57.0 | –15.2 | Ice + $NH_4H_2PO_4 \cdot 2(CH_2)_6N_4 \cdot 8H_2O$ |
| 22.0 | 21.0 | 57.0 | –17.8 | Ice + $NH_4H_2PO_4 \cdot 2(CH_2)_6N_4 \cdot 8H_2O$ + $(CH_2)_6N_4 \cdot 6H_2O$ |
| 23.0 | 15.4 | 61.6 | –14.0 | Ice + $(CH_2)_6N_4 \cdot 6H_2O$ |
| 25.7 | 7.4 | 66.9 | –12.6 | Ice + $(CH_2)_6N_4 \cdot 6H_2O$ |
| 27.5 | 4.0 | 68.5 | –11.9 | Ice + $(CH_2)_6N_4 \cdot 6H_2O$ |
| 23.0 | 23.0 | 54.0 | –11.5 | $NH_4H_2PO_4 \cdot 2(CH_2)_6N_4 \cdot 8H_2O$ + $(CH_2)_6N_4 \cdot 6H_2O$ |
| 25.0 | 26.0 | 49.0 | –4.3 | $NH_4H_2PO_4 \cdot 2(CH_2)_6N_4 \cdot 8H_2O$ + $(CH_2)_6N_4 \cdot 6H_2O$ |
| 25.6 | 27.0 | 47.4 | –2.8 | $NH_4H_2PO_4 \cdot 2(CH_2)_6N_4 \cdot 8H_2O$ + $(CH_2)_6N_4 \cdot 6H_2O$ |
| 28.7 | 28.0 | 43.3 | 18.3 | $NH_4H_2PO_4 \cdot 2(CH_2)_6N_4 \cdot 8H_2O$ + $(CH_2)_6N_4 \cdot 6H_2O$ |
| 14.0 | 25.6 | 60.4 | –4.0 | $NH_4H_2PO_4 \cdot 2(CH_2)_6N_4 \cdot 8H_2O$ + $NH_4H_2PO_4$ |
| 14.6 | 27.0 | 58.4 | 2.0 | $NH_4H_2PO_4 \cdot 2(CH_2)_6N_4 \cdot 8H_2O$ + $NH_4H_2PO_4$ |
| 16.0 | 29.2 | 54.8 | 12.0 | $NH_4H_2PO_4 \cdot 2(CH_2)_6N_4 \cdot 8H_2O$ + $NH_4H_2PO_4$ |
| 27.7 | 30.8 | 41.5 | 16.8 | $NH_4H_2PO_4 \cdot 2(CH_2)_6N_4 \cdot 8H_2O$ + $NH_4H_2PO_4$ |
| 18.9 | 32.4 | 48.7 | 20.5 | $NH_4H_2PO_4 \cdot 2(CH_2)_6N_4 \cdot 8H_2O$ + $NH_4H_2PO_4$ |
| 19.8 | 33.3 | 46.9 | 22.4 | $NH_4H_2PO_4 \cdot 2(CH_2)_6N_4 \cdot 8H_2O$ + $NH_4H_2PO_4$ |
| 22.7 | 35.0 | 42.3 | 25.5 | $NH_4H_2PO_4 \cdot 2(CH_2)_6N_4 \cdot 8H_2O$ + $NH_4H_2PO_4$ |
| 24.7 | 36.0 | 39.3 | 27.0 | $NH_4H_2PO_4$ + $(CH_2)_6N_4$ + $NH_4H_2PO_4 \cdot 2(CH_2)_6N_4 \cdot 8H_2O$ |
| 24.5 | 37.7 | 37.8 | 36.0 | $(CH_2)_6N_4$ + $NH_4H_2PO_4$ |
| 29.5 | 28.3 | 42.2 | 26.5 | $NH_4H_2PO_4 \cdot 2(CH_2)_6N_4 \cdot 8H_2O$ + $(CH_2)_6N_4$ + $(CH_2)_6N_4 \cdot 6H_2O$ |
| 31.0 | 24.1 | 44.9 | 31.0 | $(CH_2)_6N_4 \cdot 6H_2O$ + $(CH_2)_6N_4$ |
| 32.5 | 20.2 | 47.3 | 32.3 | $(CH_2)_6N_4 \cdot 6H_2O$ + $(CH_2)_6N_4$ |
| 28.4 | 18.0 | 53.6 | 32.4 | $(CH_2)_6N_4 \cdot 6H_2O$ + $(CH_2)_6N_4$ |
| 40.0 | 12.8 | 51.2 | 32.2 | $(CH_2)_6N_4 \cdot 6H_2O$ + $(CH_2)_6N_4$ |
| 40.0 | 6.0 | 54.0 | 28.5 | $(CH_2)_6N_4 \cdot 6H_2O$ + $(CH_2)_6N_4$ |

new compound can be used as a nitrogen and phosphorus fertilizer and as a corrosion inhibitor.

The X-ray diffraction patterns were recorded with a DRON-2.0 diffractometer (ω scanning). Thermal analysis was performed on a Paulik–Paulik–Erdey derivatograph in air at a heating rate of 6 deg $min^{-1}$. The IR spectra were taken on a UR-20 spectrometer. Samples were prepared as mulls in mineral oil and as KBr pellets.

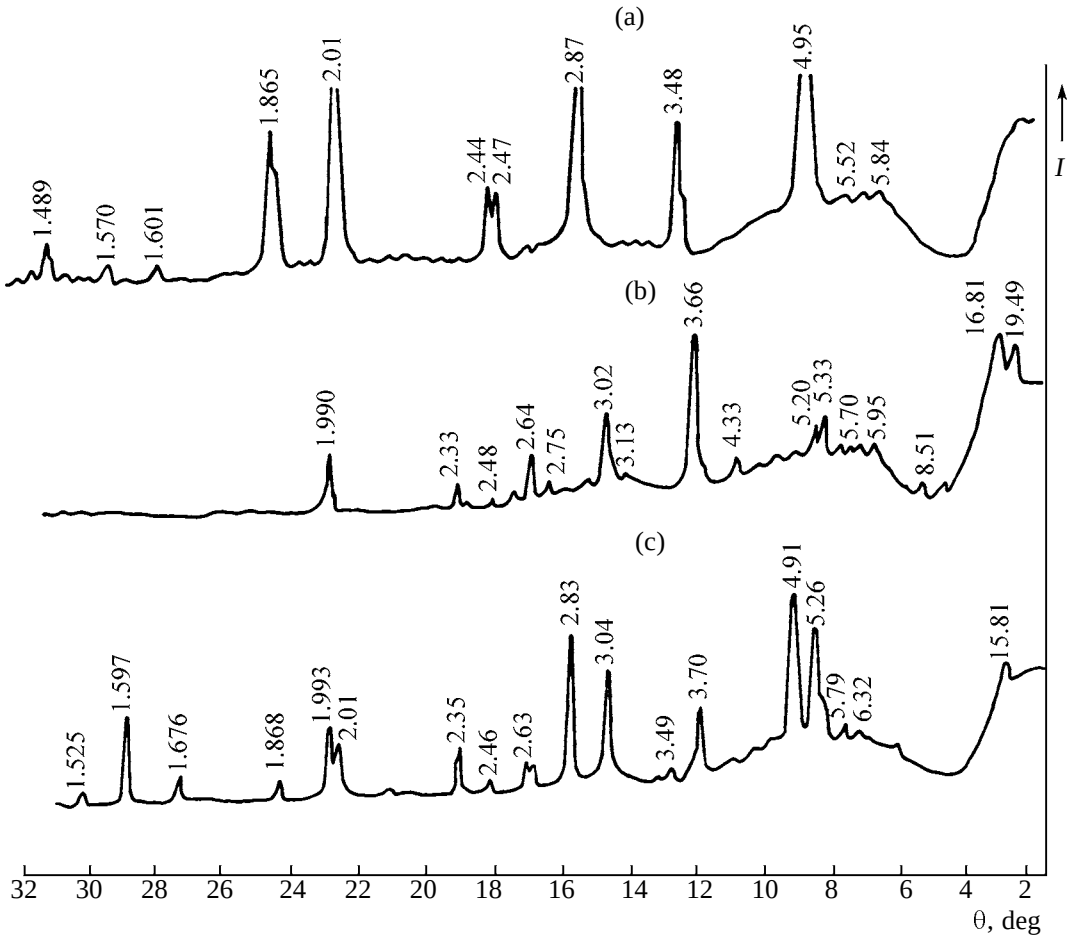


**Fig. 2.** X-ray diffraction patterns of (a) hexamethylenetetramine, (b) ammonium dihydrogen phosphate, and (c) $NH_4H_2PO_4 \cdot 2(CH_2)_6N_4 \cdot 8H_2O$. (θ) Bragg angle and (*I*) intensity. The interplanar spacings (Å) are indicated.

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