Solubility in the System NH_3–H_3PO_4–$H_4P_2O_7$–H_2O at 0° C

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In the pH range 4.1–7.7 at 0° C, solubility, expressed as % (N + P_2O_5), in the system NH_3–H_3PO_4–$H_4P_2O_7$–H_2O is higher than that in the systems NH_3–H_3PO_4–H_2O and NH_3–$H_4P_2O_7$–H_2O, and lower than that in the system NH_3–H_3PO_4–$H_4P_2O_7$–$H_5P_3O_{10}$–H_2O. In all the systems containing orthophosphate, maximum solubility is obtained at pH 5.75–5.93 and in solutions with which both $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$ are in equilibrium.

Ammonium polyphosphate fertilizers, which are mixtures of salts of ortho-, pyro-, tripoly-, tetrapoly-, and more highly condensed phosphoric acids, prepared by ammoniation of superphosphoric acid (*8, 10*), are finding increasing acceptance. In the continuing study of the properties of ammonium polyphosphates (*1, 3*), measurements were made of the compositions of solutions in the system ammonia–ortho-phosphoric acid–pyrophosphoric acid–water at 0° C with which solid phases of both phosphate species are in equilibrium over the pH range 4.05–7.76.

The equilibration mixtures were prepared from reagent mono- and diammonium orthophosphates, and di-, tri-, and tetraammonium pyrophosphates that were crystallized from liquid fertilizers produced by ammoniation of electric furnace superphosphoric acid containing 80% P_2O_5 (*9*). Stock solutions of the ammonium orthophosphates were prepared by saturating conductivity water at 5° C with the respective salts. Portions of these cold orthophosphate solutions were then saturated with the ammonium pyrophosphate expected to be the stable phase at a particular pH, and the pH of each mixture was adjusted with either anhydrous ammonia or the hydrogen form of Amberlite IR-120 resin. Cold water or solid salt was added when necessary to maintain the desired ratio of solids to liquid. No attempt was made to approach equilibrium from undersaturation. The mixtures, in plastic bottles, were equilibrated at 0.0 ± 0.5° C in a cold room with occasional manual agitation. The temperature of the cold room was controlled by a commercial thermostat and checked periodically with a standard thermometer.

Table I. The System NH_3–H_3PO_4–$H_4P_2O_7$–H_2O at 0° C

	Liquid Phase				
	Composition, %		Distribution, %, of P_2O_5		
pH	N	P_2O_5	Ortho-	Pyro-	Solid Phase[a]
7.76	9.53	25.03	44	56	B, E
7.16	10.41	29.70	45	55	B, E
6.50	11.06	32.89	41	59	B, E
6.44	11.32	34.72	36	64	B, D, E
. . .	10.97	34.83	40	60	B, D
6.24	11.08	35.23	42	58	B, D
6.10	11.06	36.11	48	52	B, D
6.06	11.06	36.09	47	53	B, D
5.97	10.84	36.55	48	52	A, D
5.93	11.07	36.87	50	50	B, D
5.93	11.06	36.83	51	49	A, B, D
5.90	11.04	36.93	50	50	B, D
5.84	10.35	36.00	41	59	A, D
5.85	10.51	36.08	43	57	A, D
5.58	10.06	35.89	42	58	A, D
5.21	9.76	36.54	28	72	A, D
5.12	9.79	37.47	32	68	A, D
5.07	9.29	36.14	25	75	A, C
5.03	9.74	37.56	24	76	A, C, D
4.83	8.74	34.91	26	74	A, C
4.68	7.53	31.46	30	70	A, C
4.05	5.06	26.23	29	71	A, C

[a] Identified by microscopic examination. A = $NH_4H_2PO_4$, B = $(NH_4)_2HPO_4$, C = $(NH_4)_2H_2P_2O_7$, D = $(NH_4)_3HP_2O_7 \cdot H_2O$, E = $(NH_4)_4P_2O_7 \cdot H_2O$.

The approach to equilibrium was followed by periodic petrographic examination of the solid phases (*5*) and by determination of the composition and pH of the liquid phases. When examination of the wet solids indicated the absence of either of the two phosphate species, a small amount of the missing species was added and equilibration was continued.

Phosphorus was determined gravimetrically as quinolinium molybdophosphate (*7*) and nitrogen was determined by distillation of ammonia with sodium hydroxide; pH was measured with a commercial meter and a glass electrode on supernatant liquid phases that had been allowed to warm to room temperature. The two phosphate species, ortho- and pyrophosphate, were determined by one-dimensional paper chromatography (*4*).

Equilibrium was established in 21–45 days. The results are summarized in Table I and plotted in Figure 1, which includes portions of the 0° C isotherms of the systems NH_3–H_3PO_4–H_2O (*6*), NH_3–$H_4P_2O_7$–H_2O (*1*), and NH_3–$H_5P_3O_{10}$–H_2O (*2*), and the quinary system NH_3–H_3PO_4–$H_4P_2O_7$–$H_5P_3O_{10}$–H_2O (*3*). The coordinates of Figure 1 were selected

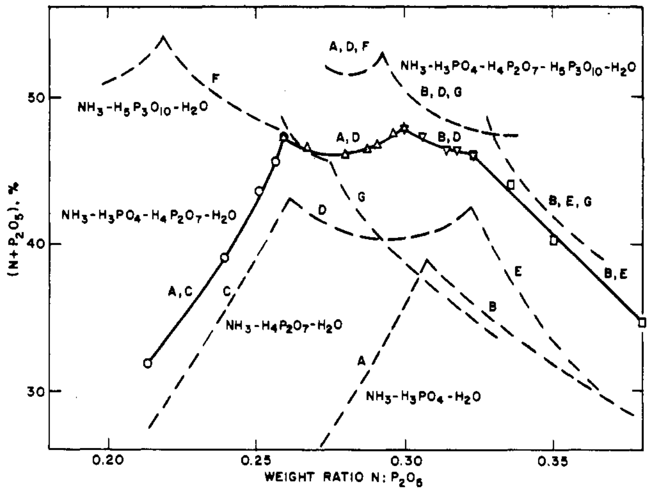

Figure 1. Solubility in ammonium phosphate systems at 0° C

A $NH_4H_2PO_4$
B $(NH_4)_2HPO_4$
C $(NH_4)_2H_2P_2O_7$
D $(NH_4)_3HP_2O_7 \cdot H_2O$
E $(NH_4)_4P_2O_7 \cdot H_2O$
F $(NH_4)_4HP_3O_{10}$
G $(NH_4)_5P_3O_{10} \cdot 2H_2O$

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to facilitate comparison of the total plant-nutrient contents, $N + P_2O_5$, of the saturated solutions in the different systems.

As shown in Figure 1, the 0° C isotherm over the pH range studied comprises four branches representing solutions saturated with the salt pairs $(NH_4)_2HPO_4 + (NH_4)_4P_2O_7\cdot H_2O$, $(NH_4)_2HPO_4 + (NH_4)_3HP_2O_7\cdot H_2O$, $NH_4H_2PO_4 + (NH_4)_3HP_2O_7\cdot H_2O$, and $NH_4H_2PO_4 + (NH_4)_2H_2P_2O_7\cdot H_2O$. These branches have slopes and contours that resemble those of the 0° C isotherms of the three ternary systems and the quinary system. At any ratio $N:P_2O_5$, the total fertilizer nutrient contents, $N + P_2O_5$, of the saturated solutions in the system NH_3–H_3PO_4–$H_4P_2O_7$–H_2O are significantly higher than those of solutions that are saturated with only ammonium orthophosphate or ammonium pyrophosphate, but are significantly lower than those of solutions saturated with ammonium ortho-, pyro-, and tripolyphosphates, particularly in the range of weight ratios $N:P_2O_5$ of 0.25–0.30 (about pH 5–6).

Properties of the three invariant solutions determined in the system NH_3–H_3PO_4–$H_4P_2O_7$–H_2O are listed in Table I. The invariant solution saturated with $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, and $(NH_4)_3HP_2O_7\cdot H_2O$ has a pH of 5.93, a value very near that (5.75) of the invariant solution of the quinary system NH_3–H_3PO_4–$H_4P_2O_7$–$H_5P_3O_{10}$–H_2O saturated with $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, $(NH_4)_3HP_2O_7\cdot H_2O$, and $(NH_4)_5P_3O_{10}\cdot 2H_2O$, and that (5.82) of the invariant solution of the ternary system NH_3–H_3PO_4–H_2O saturated with $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$. The maximum nutrient contents of the two multicomponent systems are those of the invariant solutions in which both mono- and diammonium orthophosphate are among the saturating solids.

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Solubility of PuF_3 in Molten 2 LiF-BeF_2

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The solubility of PuF_3 in molten 2 LiF-BeF_2 was determined over the temperature range of 500–660° C. The results can be expressed by the least-squares equation: $\log_{10} S(\text{mol \% } PuF_3) = 3.2305 - 3096/T(^\circ K)$. The solid phase present at equilibrium was probably pure PuF_3.

Oak Ridge National Laboratory has been engaged in the development of molten salt reactors in which the fissile material (^{235}U, ^{233}U, or ^{239}Pu) is dissolved in a molten fluoride solvent. The solvent 2 LiF-BeF_2 has been of particular interest because it was used both as the coolant and the flush salt in the Molten-Salt Reactor Experiment (MSRE) and had a composition close to that of the MSRE fuel carrier salt (*4*). In addition, Baes (*1*) used 2 LiF-BeF_2 as the reference composition in correlating thermodynamic data obtained with molten LiF-BeF_2 solutions. Barton (*2*) has measured the solubility of PuF_3 in several LiF-BeF_2 solutions ranging in BeF_2 concentration from 29 to 48 mol %. We measured the solubility of PuF_3 in molten 2 LiF-BeF_2 over the temperature range of 500–660° C; our results are summarized in this paper.

EXPERIMENTAL

Materials Used. The 2 LiF-BeF_2 used in this work was prepared by J. H. Shaffer *et al.* of the ORNL Reactor Chemistry Division. In the technique used (*6*), the appropriate amounts of LiF and BeF_2 were first melted and, then, the resulting solution was treated at about 600° C with HF-H_2 (about 10–90 mol %) followed by pure H_2. This treatment removed oxide impurities and reduced dissolved contaminants such as iron, nickel, and chromium fluorides to their respective metals. The treated solution was transferred through a sintered nickel filter into a clean nickel vessel before it was allowed to freeze. The oxide content of the purified salt was negligible, whereas the chromium, nickel, and iron concentrations were about 15, 25, and 175 ppm, respectively (*5*).

The PuF_3 powder, supplied by the Los Alamos Scientific Laboratory, was part of the same batch used by Barton (*2*). It was practically free of metallic impurities except for about 0.1% ^{241}Am, and, based on optical microscopic examination (*2*), contained less than 1% of other compounds.

Procedure. The apparatus and general technique used have been described elsewhere (*3*). Initially, 100 grams of the 2 LiF-BeF_2, contained in a molybdenum crucible, was sparged at 600° C with HF-H_2 (50-50 mol %) for about 24 hours to ensure that oxide impurities had been removed. After hydrofluorination, the salt was sparged—first with pure hydrogen, then with pure argon. With the system at 595° C under an argon atmosphere, about 6.5 grams

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