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The System NH_3–$H_5P_3O_{10}$–H_2O at 0° and 25° C.

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Measurements were made of solubility in the system NH_3–$H_5P_3O_{10}$–H_2O at 0° and 25° C. and of the hydrolysis of tripolyphosphate at 25° C. The 0° C. solubility isotherm consists of four branches in the pH range 2.5 to 8.3; the saturating phases are $(NH_4)_3H_2P_3O_{10}\cdot H_2O$, $(NH_4)_4HP_3O_{10}$, $(NH_4)_9H(P_3O_{10})_2\cdot 2H_2O$, and $(NH_4)_5P_3O_{10}\cdot 2H_2O$. At 25° C. rapid hydrolysis at low pH restricted the range in which equilibrium could be established, but in the pH range 5.1 to 8.7 the 25° C. isotherm consists of three branches; the saturating phases are $(NH_4)_9H(P_3O_{10})_2\cdot 2H_2O$, $(NH_4)_5P_3O_{10}\cdot 2H_2O$, and $(NH_4)_5P_3O_{10}\cdot H_2O$. The hydrolysis of tripolyphosphate at 25° C. in the pH range 4 to 9 is expressed by the first-order rate equation $\log\left[(P_3O_{10})_0/(P_3O_{10})_t\right] = kt$, in which t is time, days, and $k = 1.4\ (H)^{1/2}$, where H is the activity of the hydrogen ion and is calculated as $H = 10^{-pH}$.

IN THE continuing study of the properties of the ammonium polyphosphates (*1*), phase relationships in the system ammonia–tripolyphosphoric acid–water were determined at 0° C. over the pH range 2.5 to 8.3, and at 25° C. over the pH range 5.1 to 8.7. Hydrolysis of the tripolyphosphate at 25° C. also was evaluated.

The ammonium tripolyphosphates and their solutions were prepared by ammoniation and vacuum evaporation of 0.3*N* tripolyphosphoric acid that was prepared by ion exchange from solutions of recrystallized pentasodium tripolyphosphate. To minimize hydrolysis of the tripolyphosphate, all operations were carried out at temperatures below 10° C.

Techniques similar to those used in preparing the crystalline ammonium pyrophosphates (*1*) were used to prepare five ammonium tripolyphosphates. In these preparations, $(NH_4)_3H_2P_3O_{10}\cdot H_2O$ was obtained as coarse monoclinic prisms, $(NH_4)_4HP_3O_{10}$ as relatively large monoclinic plates, $(NH_4)_9H(P_3O_{10})_2\cdot 2H_2O$ as monoclinic tablets, $(NH_4)_5P_3O_{10}\cdot H_2O$ as triclinic plates, and $(NH_4)_5P_3O_{10}\cdot 2H_2O$ as monoclinic tablets. The morphological and optical properties of these salts have been published (*2*).

In the solubility study, the complexes, in capped plastic bottles, were equilibrated with occasional manual agitation in a cold room at 0° ± 0.5° C. or with mechanical rocking in a water bath at 25° ± 0.02° C. The approach to equilibrium was followed by periodic petrographic and x-ray examination of the solid phases, and by determinations of composition and pH of the liquid phases.

Phosphorus was determined gravimetrically as quinolinium molybdophosphate (*4*), and nitrogen was determined by distillation of ammonia with sodium hydroxide; pH was determined with a glass electrode in a commercial meter. Hydrolysis of the tripolyphosphates during equilibration was checked by one-dimensional paper chromatography (*3*).

Equilibrium at 0° C. was established in 26 to 120 days without significant hydrolysis. The results are summarized in Table I, and plotted in Figure 1. Two of the three invariant solutions were determined: the solution saturated with $(NH_4)_3H_2P_3O_{10}\cdot H_2O$ and $(NH_4)_4HP_3O_{10}$ at pH 3.72, and the solution saturated with $(NH_4)_9H(P_3O_{10})_2\cdot 2H_2O$ and $(NH_4)_5P_3O_{10}\cdot 2H_2O$ at pH 5.35. The solution saturated with $(NH_4)_4HP_3O_{10}$ and $(NH_4)_9H(P_3O_{10})_2\cdot 2H_2O$ was not determined but has a pH between 4.93 and 4.95 and a composition between 9.75 and 9.86% N and 37.69 and 38.09% P_2O_5.

Hydrolysis of the tripolyphosphate was significantly faster at 25° than at 0° C. and restricted the equilibrium study at 25° C. to the region of pH above 5. Equilibrium at 25° C. was established in 5 to 17 days for 10 complexes in which hydrolysis was not serious. The results are summarized in Table I and plotted in Figure 1. The saturating

Table I. The System NH_3–$H_5P_3O_{10}$–H_2O

Liquid Phase Composition, % N	 P2O5	 pH	Solid Phase
			Results at 0° C.
8.36	25.33	8.30	$(NH_4)_5P_3O_{10}\cdot 2H_2O$
9.04	30.52	5.90	$(NH_4)_5P_3O_{10}\cdot 2H_2O$
9.42	33.68	5.53	$(NH_4)_5P_3O_{10}\cdot 2H_2O$
9.83	35.69	5.35	$(NH_4)_9H(P_3O_{10})_2\cdot 2H_2O + (NH_4)_5P_3O_{10}\cdot 2H_2O$
9.75	36.66	5.19	$(NH_4)_9H(P_3O_{10})_2\cdot 2H_2O$
9.86	37.69	4.95	$(NH_4)_9H(P_3O_{10})_2\cdot 2H_2O$
9.75	38.09	4.93	$(NH_4)_4HP_3O_{10}$
9.61	40.16	4.41	$(NH_4)_4HP_3O_{10}$
9.68	43.41	4.00	$(NH_4)_4HP_3O_{10}$
9.73	44.35	3.72	$(NH_4)_3H_2P_3O_{10} + (NH_4)_4HP_3O_{10}$
8.80	42.66	3.13	$(NH_4)_3H_2P_3O_{10}$
8.38	42.36	2.51	$(NH_4)_3H_2P_3O_{10}$
			Results at 25° C.
9.30	26.30	8.72	$(NH_4)_5P_3O_{10}\cdot 2H_3O$
9.39	28.49	7.88	$(NH_4)_5P_3O_{10}\cdot 2H_2O$
9.39	28.45	7.80	$(NH_4)_5P_3O_{10}\cdot 2H_2O$
9.65	31.15	6.38	$(NH_4)_5P_3O_{10}\cdot H_2O + (NH_4)_5P_3O_{10}\cdot 2H_2O$
9.69	32.01	6.25	$(NH_4)_5P_3O_{10}\cdot H_2O$
9.72	32.43	6.02	$(NH_4)_5P_3O_{10}\cdot H_2O$
10.0	35.39	5.58	$(NH_4)_5P_3O_{10}\cdot H_2O$
10.3	36.56	5.57	$(NH_4)_5P_3O_{10}\cdot H_2O$
10.3	36.52	5.54	$(NH_4)_5P_3O_{10}\cdot H_2O$
10.4	39.79	5.12	$(NH_4)_9H(P_3O_{10})_2\cdot 2H_2O$

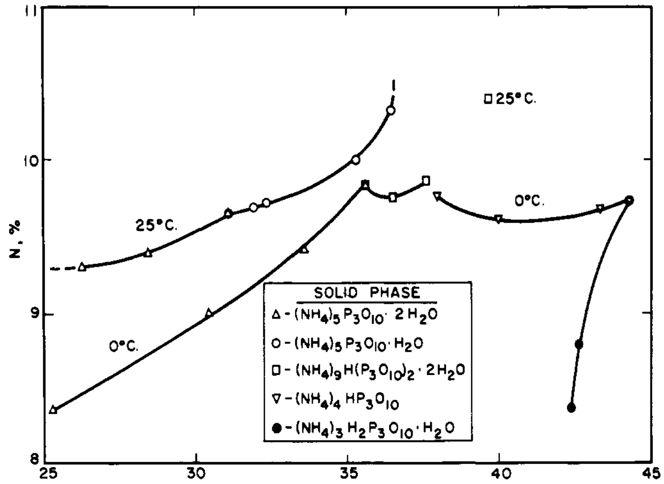

Figure 1. The system NH_3–$H_5P_3O_{10}$–H_2O at 0° and 25° C.

solid phases are $(NH_4)_9H(P_3O_{10})_2\cdot 2H_2O$, $(NH_4)_5P_3O_{10}\cdot H_2O$, and $(NH_4)_5P_3O_{10}\cdot 2H_2O$. Only the invariant solution at pH 6.38 saturated with the mono- and dihydrates of the pentaammonium salt was determined. The invariant solution saturated with $(NH_4)_9H(P_3O_{10})_2\cdot 2H_2O$ and $(NH_4)_5P_3O_{10}\cdot H_2O$ was not determined, but it probably has a pH between 5.1 and 5.5, and a P_2O_5 content between 36.5 and 39.8%.

HYDROLYSIS OF TRIPOLYPHOSPHATE AT 25° C.

Chromatographic analysis of the concentrated ammonium tripolyphosphate solutions that had partially hydrolyzed at 25° C. showed that the phosphorus present as pyrophosphate was about twice that present as orthophosphate, indicating that, in at least the early stages of its hydrolysis, tripolyphosphate hydrolyzes according to the equation

$$P_3O_{10}^{-5} + H_2O = PO_4^{-3} + P_2O_7^{-4} + 2H^- \qquad (1)$$

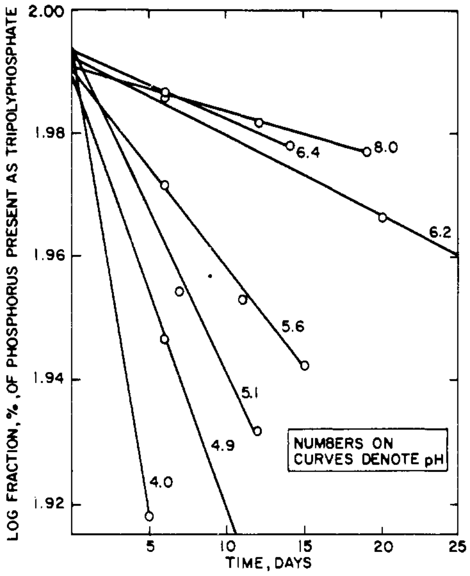

Figure 2. Hydrolysis of concentrated ammonium tripolyphosphate solutions at 25° C.

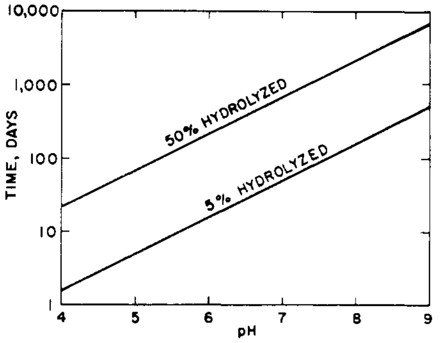

Figure 3. Effect of pH on hydrolysis of concentrated ammonium tripolyphosphate solutions at 25° C.

Plots of the data (Figure 2) showed that the hydrolysis of tripolyphosphate is first order and, at each pH, may be represented by the equation

$$-d(P_3O_{10})/dt = k(P_3O_{10}) \qquad (2)$$

which, on integration, yields

$$\log\left[(P_3O_{10})_0/(P_3O_{10})_t\right] = kt \qquad (3)$$

where t is time, days. At constant pH,

$$k = aH^b \qquad (4)$$

in which H is the hydrogen ion activity, expressed as $H = 10^{-pH}$, and a and b are constants. Least-squares treatment of the data gave $a = 1.39 \pm 0.35$, $b = 0.485 \pm 0.020$. The standard deviation of the calculated from the observed percentages of tripolyphosphate is 1.48. The hydrolysis constant k thus is a function of the square root of the hydrogen ion activity

$$\log\left[(P_3O_{10})_0/(P_3O_{10})_t\right] = 1.4H^{0.5}t \qquad (5)$$

and a change of 2 pH units changes the rate of hydrolysis by a factor of 10. This effect of pH is illustrated in Figure 3 in which the time required for hydrolysis of 5 and 50% of the total initial tripolyphosphate in concentrated solutions is shown as a function of pH.

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