Solubility in the System NH_3–H_3PO_4–$H_4P_2O_7$–H_2O at 35 and 50 °C

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The quaternary system NH_3–H_3PO_4–$H_4P_2O_7$–H_2O was studied at 35 and 50 °C to determine the solubility, expressed as weight percent N + P_2O_5, in the pH range 4–7. Three invariant solutions were determined at both temperatures. The two with the lower pH at each temperature had the highest solubility. The invariant solution containing the solid phases $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, and $(NH_4)_3HP_2O_7{\cdot}H_2O$ had an increase of 6.7% in solubility (wt % N + P_2O_5) as the temperature increased from 35 to 50 °C.

Previous studies (*1*, *2*) have shown the solubility in the quaternary system ammonia–orthophosphoric acid–pyrophosphoric acid–water at 0 and 25 °C. In the continuing study of this system, measurements were made of the compositions of solutions at 35 and 50 °C which contained both phosphate species in the solid phase over the pH range 4.0–7.3.

In the preparation of the equilibration mixtures, reagent monoammonium and diammonium salts were used as the source of orthophosphate. The di-, tri-, and tetraammonium pyrophosphates were crystallized from liquid fertilizers produced by ammoniation of 80% P_2O_5 electric-furnace superphosphoric acid (*3*). The purity of the ammonium pyrophosphate used in this study is given in Table I. Stock solutions of the ammonium orthophosphates were prepared by saturating distilled water at 5 °C above the temperature of the study with the respective salts. Portions of these orthophosphate solutions (supersaturated with respect to the equilibrium temperature) then were saturated with the ammonium pyrophosphate (*4*) expected to be the stable phase for the predetermined pH of the solution. The pH of each solution was adjusted to its predetermined value with anhydrous ammonia or orthophosphoric acid.

These ammonium orthopyrophosphate complexes were placed in screw-top culture tubes and equilibrated in a water bath thermostated to a precision of ±0.1 °C at 35 or 50 °C with periodic manual agitation. The approach to equilibrium was followed by petrographic examination of the solid phase (*5*). Any missing species was added and equilibration continued. When successive examinations indicated that the solid phase was unchanged, two independent samples of the liquid phase were taken for measurement of pH and composition.

Determination of nitrogen was made by distillation of ammonia with sodium hydroxide, and phosphorus was determined gravimetrically as quinolinium molybdophosphate (*6*). The orthophosphate was determined spectrophotometrically by using the molybdovanadophosphate method (*7*). The pH was measured with a commercial meter, standardized at the equilibration temperature, using a glass electrode.

Table I. Analysis of Ammonium Pyrophosphates

salt	composn, wt % N	composn, wt % P_2O_5	distribn of phosphates, % of tot P_2O_5 ortho	distribn of phosphates, % of tot P_2O_5 pyro
$(NH_4)_4P_2O_7$	22.73	57.64	0.8	99.2
$(NH_4)_3HP_2O_7{\cdot}H_2O$	17.04	57.44	0.3	99.7
$(NH_4)_2H_2P_2O_7$	13.18	66.93	0.9	99.1

Table II. System NH_3-H_3PO_4-$H_4P_2O_7$-H_2O at 35 °C

pH	composition, wt % N	composition, wt % tot P_2O_5	composition, wt % ortho P_2O_5	solid phases[a]
4.17	7.97	37.21	12.5	A, C
4.70	9.00	39.51	13.5	A, C
5.14	10.97	43.22	12.1	A, C
5.19	11.67	45.05	12.6	A, C, D
5.61	11.40	42.91	14.3	A, D
5.87	11.88	42.59	13.7	A, D
5.89	12.70	43.88	20.3	A, B, D
6.09	12.72	43.36	19.8	B, D
6.20	12.61	42.23	18.0	B, D
6.21	12.76	42.42	16.7	B, D, E
6.48	12.56	40.79	15.8	B, E
6.53	12.40	39.52	15.8	B, E
7.18	11.53	33.26	14.8	B, E
7.33	11.34	31.96	14.7	B, E

[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 = $(NH_4)_4P_2O_7$.

Table III. System NH_3-H_3PO_4-$H_4P_2O_7$-H_2O at 50 °C

pH	composition, wt % N	composition, wt % tot P_2O_5	composition, wt % ortho P_2O_5	solid phases[a]
4.09	9.40	42.02	14.8	A, C
4.12	9.70	42.85	13.5	A, C
4.62	10.90	45.13	13.0	A, C
5.03	12.50	47.79	13.6	A, C, D
5.36	12.80	47.01	17.1	A, D
5.54	12.90	46.81	17.7	A, D
5.64	13.20	47.05	18.2	A, D
5.80	13.40	46.98	20.0	A, B, D
5.82	13.30	46.28	19.4	B, D
5.88	13.30	45.75	18.4	B, D
5.96	13.30	45.65	19.0	B, D, E
6.09	13.10	44.55	18.4	B, E
6.18	12.90	42.99	17.8	B, E
6.51	12.50	39.39	18.4	B, E
7.15	11.60	32.83	14.9	B, E
7.37	11.40	31.66	15.8	B, E

[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 = $(NH_4)_4P_2O_7$.

The results, which are the average of two independent samplings, are summarized in Tables II and III and shown in Figure 1, which includes the isotherms of the same system at 0 and 25 °C. In Figure 1 the unit on the ordinate is total plant food (wt % N + P_2O_5), which is a function of solubility. The unit on the abscissa is the weight percent ratio N:P_2O_5, which is a function of pH. In the pH range studied, both isotherms

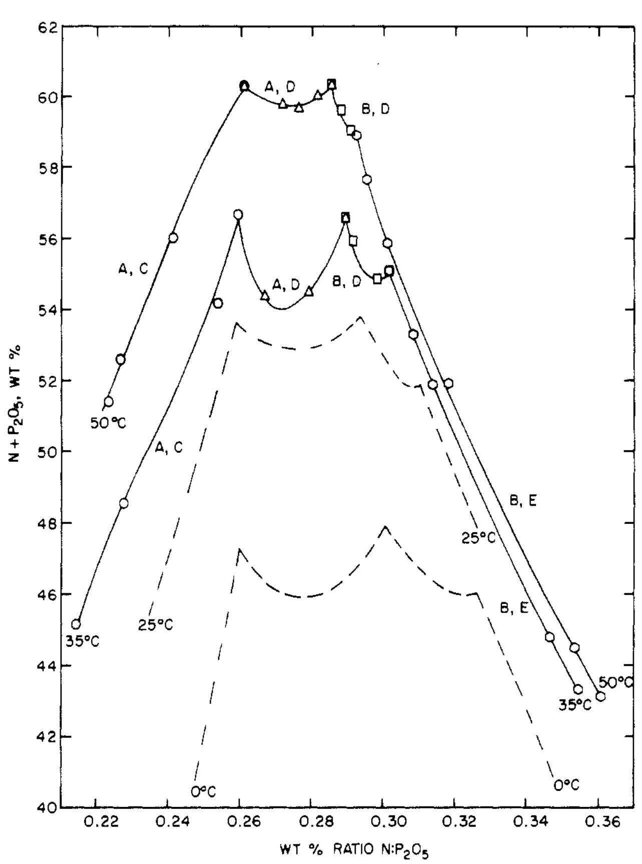

Figure 1. Solubility in ammonium ortho- and pyrophosphate systems at 35 and 50 °C [saturating solids: A = $NH_4H_2PO_4$, B = $(NH_4)_2HPO_4$, C = $(NH_4)_2H_2P_2O_7$, D = $(NH_4)_3HP_2O_7\cdot H_2O$, E = $(NH_4)_4P_2O_7$].

comprise four branches representing the salt pairs $NH_4H_2PO_4$ and $(NH_4)_2H_2P_2O_7$, $NH_4H_2PO_4$ and $(NH_4)_3HP_2O_7\cdot H_2O$, $(NH_4)_2HPO_4$ and $(NH_4)_3HP_2O_7\cdot H_2O$, and $(NH_4)_2HPO_4$ and $(NH_4)_4P_2O_7$.

The composition of three invariant solutions was determined at both temperatures. The three salts found at the three invariant points were $NH_4H_2PO_4$, $(NH_4)_2H_2P_2O_7$, and $(NH_4)_3HP_2O_7\cdot H_2O$; $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, and $(NH_4)_3HP_2O_7\cdot H_2O$; and $(NH_4)_2HPO_4$, $(NH_4)_3HP_2O_7\cdot H_2O$, and $(NH_4)_4P_2O_7$. The most concentrated solutions ($N + P_2O_5$) are found in the region adjacent to the two invariant points with the lowest pH. In those two invariant points with the highest pH, there is a pronounced decrease in the ratio $N:P_2O_5$ as the temperature increases. In the invariant solutions with the lowest pH, the ratio $N:P_2O_5$ remains essentially constant over the temperature range 0-50 °C.

Registry No. NH_3, 7664-41-7; H_3PO_4, 7664-38-2; $H_4P_2O_7$, 2466-09-3.

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Adsorption of Ethylene/Ethane Mixtures on a Carbon Molecular Sieve

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Adsorption equilibria for the system of ethylene-ethane-carbon molecular sieve (MSC·5A) were measured at temperatures (and pressures) of 10 °C (0.67, 2.67, 4.00, 6.67, 13.33, and 20.00 kPa), 20 °C (0.67, 2.00, 5.33, and 10.67 kPa), and 40 °C (0.67, 3.33, 9.33, and 22.66 kPa). The adsorption isotherms of pure ethylene and ethane were determined at 10, 20, 30, and 40 °C at pressures of 1.5-47 kPa. Henry's law was not applicable to the adsorption in the low-pressure region because of the existence of high-energy sites from which the adsorbed molecules cannot be removed reversibly in the micropores.

Introduction

Adsorption equilibrium data for multicomponent gaseous mixtures are essential for designing adsorption plants, and the data are also of interest for the thermodynamics of adsorption. The solid adsorbents often have heterogeneous surfaces and are rich in micropores. Although the actual separation of gases are made at comparatively high pressures, the thermodynamical interest for the prediction calculation from the pure isotherms exists in the adsorption at low pressures where the heterogeneity and the characteristics of micropores appear significantly. In this study we measured the adsorption equilibrium data for binary gaseous mixtures of ethylene and ethane on a carbon molecular sieve (MSC·5A) at temperatures (and pressures) of 10 °C (0.67, 2.67, 4.00, 6.67, 13.33, and 20.00 kPa), 20 °C (0.67, 2.00, 5.33, and 10.67 Pa), and 40 °C (0.67, 3.33, 9.33, and 22.66 kPa). The adsorption isotherms of the pure components also were determined at 10, 20, 30, and 40 °C and at pressures from 1.5 to 47 000 Pa. The adsorption equilibrium data at 30 °C for this binary gaseous system were previously reported (*1*).

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