Ammonia–Phosphoric Acid–Water System at 25° C.

Density, Viscosity, pH, Conductance, Vapor Pressure

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PHYSICOCHEMICAL data on aqueous phosphate systems (*10, 17*) are extended here by information on the density, viscosity, pH, electrical conductance, and partial pressures of water and ammonia of solutions in the system ammonia-phosphoric acid-water at 25° C.

Solubilities in the system are reported fully in the literature (*5, 11, 14, 15, 19*). Data on vapor pressures (*6, 9, 16*), pH (*1*), and conductances (*21*) of the solutions are few, although vapor pressures (*8*), densities (*3*), and viscosities (*7*) of phosphoric acid solutions are reported.

The present study covers solutions containing up to 50% H_3PO_4 and having mole ratios NH_3:H_3PO_4 up to 11.5.

PREPARATION OF SOLUTIONS

Most of the solutions were prepared from reagent grades of phosphoric acid and ammonium hydroxide, a laboratory preparation of monoammonium phosphate (from cylinder ammonia and reagent-grade phosphoric acid), and distilled water. Saturated solutions at various mole ratios NH_3:H_3PO_4 above 0.5 and solutions containing 50% H_3PO_4 at mole ratios NH_3:H_3PO_4 Of 0.1, 0.2, and 0.3 were diluted with distilled water to traverse the line between the concentrated solution and the water corner.

Most of the solutions were analyzed precisely for ammonia and phosphorus, but some of the more dilute solutions were prepared by weight dilution of more concentrated solutions with conductance water. All the solutions with mole ratios NH_3:H_3PO_4 of 0.1 and 0.2 (used only for determinations of conductance, density, and pH) were prepared with conductance water. The compositions of the solutions in the present study are superimposed in Figure 1 upon a plot of the solubility isotherm at 25° C. as derived from published data (*5, 11, 14, 15, 19*).

MEASUREMENTS

Density. Density was measured with 25-ml. pycnometers of the modified Gay-Lussac type.

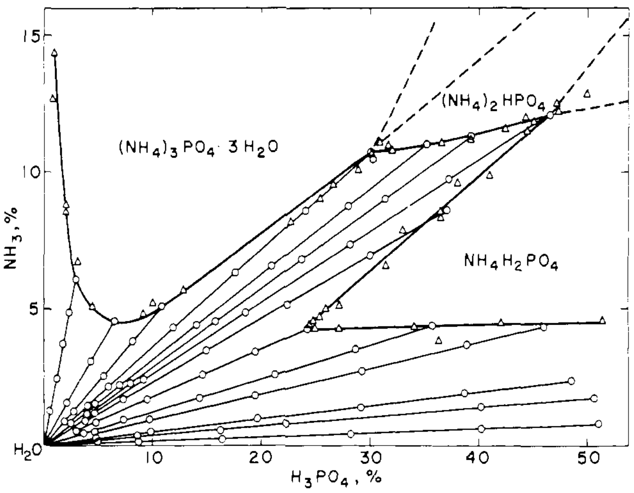

Figure 1. System NH_3-H_3PO_4-H_2O at 25° C.
△ Solubility data (*5, 11, 14, 15, 19*)
○ Solutions examined in this study

Viscosity. Viscosity was measured with Cannon-Fenske routine viscometers that were calibrated with water as the primary standard. The viscosity of water at 25° C. was calculated (*4*) to be 0.8902 centipoise from the reliable value at 20° C. (*18*).

pH. pH was measured with a glass electrode in a portable pH meter (Leeds & Northrup, Model 7661).

Conductance. Electrical conductance was measured with the equipment and by the methods of Mason and Culvern (*13*). Readings were corrected for calibration of the electrical bridge. The cells were standardized with solutions of potassium chloride, thrice crystallized from water and fused (*12*). The temperature of the oil bath was measured with a Beckman thermometer which was checked against a platinum resistance thermometer calibrated by the National Bureau of Standards.

Table I. Density, Viscosity, pH, Conductance, and Vapor Pressure

Mole Ratio	Compn., %		Molality		Density,		Viscosity,	Conductance		Partial Pressure, Mm. Hg.	
NH_3:H_3PO_4	NH_3	H_3PO_4	NH_3	H_3PO_4	Grams/Ml.	pH	Cps.	Specific, ohm^{-1} cm.$^{-1}$	Molar, ohm^{-1}	NH_3	H_2O
11.54	6.09	3.02	3.93	0.34	1.0009	10.54	1.092	0.031361	101.6760	50.541	22.519
	4.84	2.42	3.07	0.27	1.0000	10.42	1.046	0.027574	111.6633	38.428	22.956
	3.65	1.82	2.27	0.20	0.9993	10.37	1.005	0.023039	124.3920	27.177	23.211
	2.43	1.22	1.43	0.12	0.9987	10.30	0.964	0.017356	139.5985	16.995	23.484
	1.22	0.61	0.73	0.06	0.9984	10.18	0.927	0.010395	167.2693	7.260	23.643
3.97	4.53	6.60	2.99	0.76	1.0432	10.00	1.246	0.059891	85.2464	24.237	23.011
	3.04	4.40	1.93	0.49	1.0281	9.89	1.101	0.046709	101.1902	14.389	23.155
	1.52	2.20	0.93	0.23	1.0127	9.78	0.987	0.028656	126.0486	6.443	23.542
2.69	5.08	10.91	3.55	1.33	1.0839	9.62	1.547	0.084025	69.6339	15.632	22.765
	3.80	8.15	2.53	0.95	1.0620	9.58	1.312	0.072270	81.8280	10.408	23.010
	2.55	5.44	1.63	0.60	1.0406	9.50	1.138	0.056040	97.0164	6.270	23.353
	1.28	2.72	0.78	0.29	1.0191	9.40	1.002	0.034181	120.8440	2.857	23.543
	0.86	1.83	0.52	0.19	1.0120	9.17	...	0.025233	133.5224	...	...
2.05	10.72	30.02	10.62	5.17	1.2465	8.70	6.793	0.096189	25.1912	4.260	21.198
	8.57	24.07	7.47	3.65	1.1964	8.68	3.765	0.110019	37.4405	3.424	21.966
	6.39	17.98	4.96	2.43	1.1460	8.64	2.336	0.109518	52.0880	2.455	22.461
	4.29	12.01	3.01	1.46	1.0969	8.60	1.584	0.093596	69.6263	1.512	22.961
	2.14	6.01	1.37	0.67	1.0475	8.42	1.153	0.061061	95.0520	0.686	23.335
	1.44	4.02	0.89	0.43	1.0311	8.38		0.045875	108.4619	...	...
	0.71	2.00	0.43	0.21	1.0142	8.23	...	0.026894	129.9355	...	...

Table I. Continued

Mole Ratio NH_3:H_3PO_4	Compn., %		Molality		Density, Grams/Ml.	pH	Viscosity, Cps.	Conductance		Partial Pressure, Mm. Hg	
	NH_3	H_3PO_4	NH_3	H_3PO_4				Specific, $ohm^{-1} cm.^{-1}$	Molar, ohm^{-1}	NH_3	H_2O
1.98	10.41	30.32	10.31	5.22	1.2479	8.08	6.662	0.097929	25.3646	1.216	21.238
1.79	10.99	35.24	12.00	6.69	1.2805	6.84	9.001	0.095452	20.7298	0.095	20.629
	8.73	28.20	8.13	4.56	1.2230	6.88	4.564	0.113617	32.2845	0.068	21.669
	6.54	21.17	5.31	2.99	1.1661	6.92	2.649	0.115875	46.0001	0.056	22.346
	4.40	14.17	3.17	1.78	1.1097	7.00	1.649	0.099788	62.1910	0.050	22.807
	2.19	7.04	1.42	0.79	1.0537	7.03	1.187	0.064822	85.6369	0.030	23.240
	1.48	4.75	0.93	0.52	1.0358	7.08	...	0.048776	97.1535	...	...
	0.73	2.35	0.44	0.25	1.0166	7.19	...	0.028496	116.8944	...	...
1.65	11.30	39.34	13.44	8.13	1.3086	6.38	11.914	0.089213	16.9829	0.034	20.069
	9.00	31.58	8.89	5.42	1.2453	6.47	5.464	0.112897	28.1334	0.025	21.381
	6.80	23.63	5.74	3.47	1.1820	6.50	2.947	0.118490	41.5745	0.022	22.271
	4.53	15.77	3.34	2.02	1.1197	6.58	1.794	0.102974	57.1505	0.022	22.799
	2.26	7.91	1.48	0.90	1.0587	6.67	1.215	0.067054	78.4692	0.013	23.392
	1.15	3.99	0.71	0.43	1.0292	6.82	...	0.040603	96.8974	...	...
	0.57	2.01	0.34	0.21	1.0134	6.90	...	0.023625	113.6654	...	...
1.50	12.08	46.56	17.15	11.49	1.3604	5.82	21.794	0.070947	10.9769	0.016	18.718
	9.70	37.34	10.76	7.19	1.2853	5.90	7.998	0.106066	21.6583	0.013	20.712
	7.29	27.91	6.61	4.40	1.2104	6.00	3.675	0.120248	34.8831	0.012	21.913
	4.86	18.63	3.73	2.49	1.1376	6.15	2.014	0.108312	50.0841	0.008	22.663
	2.43	9.33	1.62	1.08	1.0673	6.33	1.270	0.071664	70.5276	0.005	23.181
	1.21	4.65	0.76	0.50	1.0328	6.50	...	0.043043	87.8337	...	...
	0.61	2.34	0.37	0.25	1.0146	6.64	...	0.025011	103.2381	...	...
1.33	8.58	37.13	9.28	6.98	1.2760	5.30	6.589	0.112342	23.2377	0.002	20.921
	6.92	29.78	6.42	4.80	1.2173	5.44	3.062	0.119499	32.3049	...	21.813
	5.18	22.31	4.20	3.14	1.1601	5.60	2.333	0.112262	42.5073	...	22.404
	3.45	14.86	2.48	1.86	1.1044	5.76	1.578	0.091059	54.3756	...	22.893
	1.71	7.47	1.11	0.84	1.0509	6.00	1.213	0.056649	70.7190	...	23.475
	0.87	3.77	0.54	0.40	1.0245	6.23	...	0.033481	84.9508	...	...
	0.43	1.86	0.26	0.19	1.0107	6.42	...	0.018864	98.3388	...	...
1.01	4.25	24.27	3.49	3.47	1.1632	4.00	2.269	0.101040	35.0748	...	22.153
	3.39	19.40	2.58	2.56	1.1284	4.13	1.786	0.091109	40.7871	...	22.508
	2.56	14.58	1.81	1.80	1.0948	4.30	1.453	0.076986	47.2656	...	22.841
	1.70	9.73	1.13	1.12	1.0618	4.51	1.209	0.058270	55.2731	...	23.136
	0.85	4.86	0.53	0.53	1.0294	4.80	1.029	0.034124	66.8445	...	23.466
	0.57	3.27	0.35	0.35	1.0189	...	...	0.024623	72.4249	...	...
	0.28	1.63	0.17	0.17	1.0079	...	...	0.013547	80.8087	...	...
0.70	4.36	35.76	4.28	6.09	1.2392	1.82	3.751	0.126882	28.0600	...	21.325
	3.50	28.60	3.03	4.30	1.1860	1.89	2.562	0.114701	33.1392	...	21.926
	2.64	21.46	2.04	2.89	1.1359	2.01	1.840	0.094443	37.9687	...	22.480
	1.75	14.32	1.22	1.74	1.0877	2.10	1.387	0.069078	43.4624	...	22.971
	0.88	7.19	0.56	0.80	1.0420	2.20	1.096	0.039530	51.7078	...	23.375
	0.44	3.61	0.27	0.38	1.0196	...	...	0.022428	59.7138	...	...
	0.23	1.84	0.14	0.19	1.0084	...	...	0.012762	67.4037	...	...
0.54	4.32	46.10	5.12	9.49	1.3160	1.00	6.231	0.141063	22.7867	...	19.673
	3.62	38.94	3.70	6.92	1.2580	1.15	4.090	0.137717	27.5510	...	20.857
	2.70	29.20	2.33	4.38	1.1850	1.43	2.485	0.117347	33.2351	...	21.914
	1.82	19.51	1.36	2.53	1.1187	1.63	1.648	0.085067	38.1959	...	22.646
	0.91	9.76	0.60	1.12	1.0562	1.83	1.176	0.046928	44.6126	...	23.243
	0.45	4.85	0.28	0.52	1.0261	2.05	...	0.026243	51.6781	...	...
	0.15	1.63	0.09	0.17	1.0069	2.23	...	0.011071	66.1076	...	...
0.28	2.35	48.56	2.81	10.09	1.3266	0.00	5.729	0.166685	25.3574	...	18.546
	1.87	38.81	1.85	6.68	1.2486	0.38	3.527	0.157228	31.7972	...	20.484
	1.41	29.12	1.19	4.28	1.1781	0.72	2.295	0.127009	36.2817	...	21.782
	0.94	19.44	0.69	2.49	1.1131	1.00	1.587	0.086248	39.0611	...	22.638
	0.47	9.75	0.31	1.11	1.0534	1.30	1.159	0.044840	42.7852	...	23.328
	0.24	4.86	0.15	0.52	1.0249	...	...	0.025083	49.3502	...	...
	0.08	1.61	0.05	0.17	1.0063	1.83	...	0.011323	68.4929	...	...
0.19	1.70	50.59	2.09	10.82	1.3432	0.00	...	0.180689	26.0586	...	...
	1.36	40.50	1.37	7.11	1.2604	0.12	...	0.174361	33.4743	...	...
	0.74	22.17	0.56	2.94	1.1297	0.72	...	0.104444	40.8679	...	...
	0.55	16.25	0.39	1.99	1.0918	0.96	...	0.075957	41.9562	...	...
	0.29	8.65	0.19	0.97	1.0463	1.14	...	0.041871	45.3385	...	...
	0.15	4.53	0.09	0.49	1.0226	1.38	...	0.024615	52.0739	...	...
	0.07	2.08	0.04	0.22	1.0089	1.60	...	0.014160	66.1272	...	...
0.09	0.79	51.13	0.96	10.82	1.3432	< 0	...	0.204701	29.1816	...	...
	0.62	40.36	0.62	6.98	1.2575	< 0	...	0.198398	38.3093	...	...
	0.44	28.10	0.36	4.01	1.1677	0.29	...	0.149659	44.6984	...	...
	0.26	16.42	0.18	2.01	1.0923	0.52	...	0.086657	47.3493	...	...
	0.13	8.61	0.08	0.96	1.0460	0.95	...	0.046822	50.9494	...	...
	0.07	4.59	0.04	0.49	1.0225	1.23	...	0.027416	57.2469	...	...
	0.033	2.09	0.02	0.22	1.0087	1.43	...	0.015605	72.5401	...	...

Vapor Pressure. Partial pressures of water and ammonia were measured by a dynamic method (*2*). The glass saturator was packed with glass helices. With the more viscous solutions, rates of oscillation of the saturator were as low as two per minute. With solutions that had appreciable pressures of ammonia, a presaturator prevented significant change in the composition of the solution during a measurement.

The two storage bulbs in the displacement meter held 6 liters each. Dried, carbon dioxide-free nitrogen from the bulbs was passed through the saturator at a rate of about 100 cc. per minute; four bulbfuls of gas were used in each determination.

The gas from the saturator was passed through U-tube absorbers, each containing about 3 grams of anhydrous magnesium perchlorate. Two bulbs in series were used in most of the runs—three when the amount of ammonia was large. The tubes were weighed before and after each run, the absorbent was dissolved in water made slightly acidic with sulfuric acid, and the ammonia was determined precisely. Water vapor was determined by difference.

RESULTS

In correlating the results (Table I) molar conductances were calculated on the basis of the phosphoric acid content. Plots of molar conductance against mole ratio $NH_3:H_3PO_4$ at constant molalities of phosphoric acid (Figure 2) show a dip in the conductance at a mole ratio $NH_3:H_3PO_4$ of 1, which corresponds to monoammonium phosphate. Similar plots of the partial pressure of water (Figure 3) show a similar dip at a mole ratio $NH_3:H_3PO_4$ of 1. In each series of plots, the dip becomes more pronounced as the concentration is increased to 3.5 molal H_3PO_4, the concentration corresponding to a saturated solution of monoammonium phosphate.

The partial pressures of water vapor measured in this work are somewhat higher than those reported by Huey and Tartar (*9*) but are more consistent with the vapor pressures of phosphoric acid solutions reported by Elmore, Mason, and Christensen (*8*).

The partial pressure of ammonia is very low at mole ratios $NH_3:H_3PO_4$ less than 2, which corresponds to diammonium phosphate. The partial pressures of ammonia measured in this work are somewhat lower than those reported by Huey and Tartar (*9*), although the two sets of results yield curves similar in shape—both in disagreement with Roehl's assertion (*16*), based on Warren's data (*20*), that the pressure of ammonia over saturated solutions of diammonium phosphate is inappreciable at temperatures below 55° C. As shown in Table I, for example, the partial pressure of ammonia at 25° C. is 4.26 mm. of mercury over a substantially saturated solution 5.17 molal in phosphoric acid and having a mole ratio $NH_3:H_3PO_4$ of 2.05.

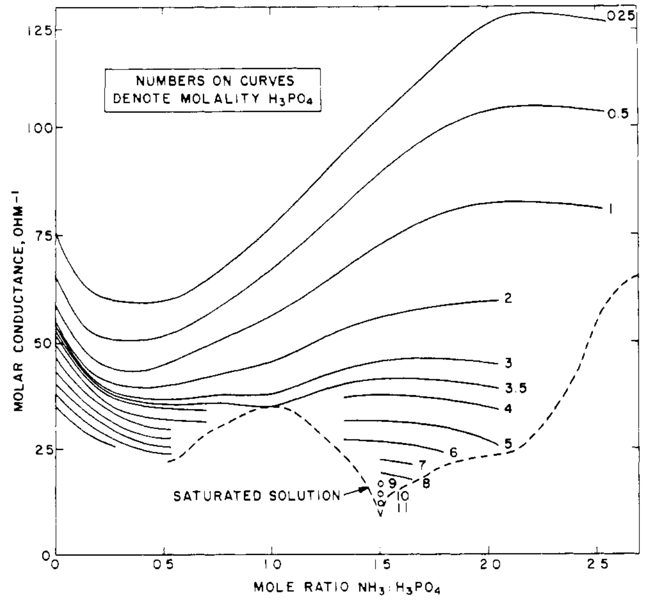

Figure 2. Molar condustance in the NH_3-H_3PO_4-H_2O system at 25° C.

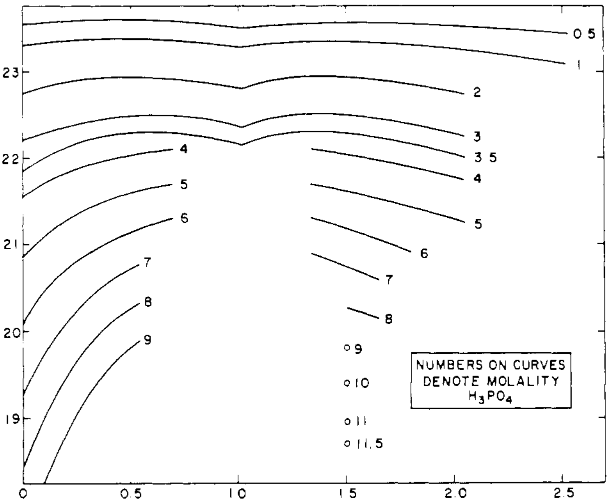

Figure 3. Partial pressure of water

The results reported in Table I for viscosity, density, and condustance probably are accurate within the limits of error of the analyses of the solutions. The vapor pressure data are less accurate; measurements on the same solution agreed within 0.5% for the partial pressure of water and within 1% for the partial pressure of ammonia at values upward from 1 mm. of mercury.

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