Selected Aqueous Phase Diagrams of Condensed Phosphate Systems

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Aqueous phase diagrams were determined for the following systems: $Na_4P_4O_{12}$–$Na_3P_3O_9$–H_2O; $Na_3P_3O_9$–$Na_4P_2O_7$–H_2O; $Na_5P_3O_{10}$–$K_5P_3O_{10}$–H_2O; $Na_5P_3O_{10}$–$Na_2B_4O_7$–H_2O; $Na_5P_3O_{10}$–Na_2SO_4–H_2O; $Na_5P_3O_{10}$–Na_2SiO_3–H_2O and $Na_5P_3O_{10}$–$(NH_2)_2CO$–H_2O at 30° C. A new series of solid solutions was discovered in the $Na_5P_3O_{10}$–$K_5P_3O_{10}$–H_2O system.

ALTHOUGH phase diagrams for the solid-melt systems of condensed phosphates are numerous, relatively few aqueous phase diagrams have been determined for these systems (*1*). Perhaps this has resulted from the belief that condensed phosphates are too unstable in aqueous solution to be considered as candidates for aqueous phase studies. Many of the poly- and metaphosphates suffer only small amounts of degradation in aqueous solutions in the time required to obtain solubility equilibrium, provided the pH and temperature conditions are not extreme. There is sufficient degradation to cause some difficulties in obtaining reproducible analytical data from these systems.

EXPERIMENTAL

The chemicals used in this work were either reagent grade or were laboratory preparations which were purified by the more or less standard methods employed in phosphate chemistry (*2*).

The samples for the phase studies were prepared by mixing 50-gram total sample in 60 ml. bottles at a predetermined ratio on a tie line near the expected liquidus line—that is to say, the samples were usually rich in the liquid phase. The samples were then placed in a thermostatically controlled bath at 30.00° ±0.01° C., and shaken vigorously several times each day for 5 days. Then they were analyzed to obtain a preliminary phase diagram.

The preliminary diagram was obtained from analyses of the water contained in the liquid phases and the compositions of the samples used to prepare the diagram. The quantity of water in the liquid phase was determined by the ZnO fusion method (*3*). Very little difficulty was encountered in applying this technique when it was applicable.

To check the preliminary diagrams a completely new set of samples were prepared and allowed to remain in the thermostatically controlled bath for 14 or more days. These samples were then analyzed for all components in the liquid phase, and selected samples were analyzed by the wet residue method (*4*).

All of the analytical procedures were routine as cited in the references with the exception of the analyses used for the $Na_3P_3O_9$–$Na_4P_4O_{12}$–H_2O and the $K_5P_3O_{10}$–$Na_5P_3O_{10}$–H_2O systems. The chemical similarity of the ring metaphosphates causes them to be difficult to analyze. Paper chromatography was used for these analyses (*5*, *6*). In this instance, the preliminary phase diagram based upon the ZnO fusion analysis only is as reliable as the more detailed diagram. The analyses of the $Na_5P_3O_{10}$–$K_5P_3O_{10}$–H_2O system depend upon flame photometry (*7*) for Na_2O and K_2O, because there is no good method for the specific species, $K_5P_3O_{10}$ or $Na_5P_3O_{10}$. The preliminary diagram was not very useful in this case, because the solid solutions which form in the system cannot be represented by a fixed point on the diagram.

The makeup data and analytical data used to construct the diagrams are shown in Tables I, II, and III. The errors committed in the analytical data vary from system

Table I. Starting Compositions and Analyses of the Ternary Systems

Initial Composition, Wt. %			Saturated Liquor, Wt. %			
$Na_4P_4O_{12}$	$Na_3P_3O_9$	H_2O	$Na_4P_4O_{12}$	$Na_3P_3O_9$	H_2O	
			13.10		86.90	
12.95	2.11	84.94	11.08	2.89	86.03	
9.93	6.05	84.02	9.76	5.29	84.95	
8.04	10.05	81.91	9.50	7.36	83.14	
6.01	14.01	79.97	5.82	12.89	81.29	
6.02	18.03	75.95	4.86	17.04	78.10	
5.01	21.03	73.96	4.27	19.70	76.03	
5.01	23.02	71.97	3.44	19.91	76.65	
3.01	25.18	71.81	3.35	19.93	76.72	
0.94	25.88	73.18	1.82	20.72	77.46	
. . .	25.00	75.00	. . .	22.33	77.67	
$Na_4P_2O_7$	$Na_3P_3O_9$	H_2O	$Na_4P_2O_7$	$Na_3P_3O_9$	H_2O	
10.00	. . .	90.00	7.04	. . .	92.96	
10.00	2.00	88.00	5.99	1.85	92.16	
7.99	6.00	86.01	4.36	6.05	89.59	
6.97	9.96	83.07	3.63	10.35	86.02	
6.97	13.93	79.11	3.34	14.60	82.06	
7.01	17.03	75.97	3.40	17.78	78.82	
7.00	20.00	72.99	3.61	20.93	75.46	
4.01	21.99	74.00	3.57	20.53	75.90	
2.00	23.00	75.00	2.42	20.86	76.72	
1.00	22.97	76.03	1.39	21.34	77.27	
. . .	25.00	75.00	. . .	22.33	77.67	
$Na_5P_3O_{10}$[a]	$K_5P_3O_{10}$	H_2O	$Na_5P_3O_{10}$	$K_5P_3O_{10}$	H_2O by Difference	H_2O(LOI)
21.00	3.00	76.00	16.75	3.47	79.78	80.55
21.00	9.00	70.00	19.33	9.40	71.27	71.55
21.00	14.00	65.00	20.45	14.18	65.37	65.81
21.00	19.00	60.00	20.81	19.42	59.77	60.69
20.96	23.96	55.08	20.10	24.65	55.25	56.07
21.00	29.00	50.00	18.91	29.59	51.50	51.20
20.95a	33.92	45.13	18.06	34.61	47.33	47.31
20.96	38.93	40.12	16.75	41.77	41.48	43.38
19.16	35.33	45.28	17.49	35.64	46.87	46.49
16.81	41.13	42.06	15.86	39.36	44.78	42.83
16.01	42.38	41.61	13.62	41.12	45.26	45.06
14.60	44.04	41.36	14.41	43.60	41.99	41.85
12.70	45.37	41.93	11.96	43.72	44.31	43.78
11.91	48.00	40.09	11.60	46.61	41.79	40.73
10.00b	49.98	40.02	8.26	52.08	39.66	41.52
8.64	52.31	39.06	7.54	49.19	43.36	39.50
6.47	55.49	38.04	5.54	54.19	40.27	38.88
5.12c	57.36	37.51	4.25	57.07	38.68	38.45
3.74d	60.74	35.52	2.96	59.82	37.22	36.14
2.17	63.84	33.99	1.91	63.53	34.56	34.56

[a] Wet residue analyses, wt. %.

	$Na_5P_3O_{10}$	$K_5P_3O_{10}$	H_2O
a	55.42	29.92	14.66
b	22.47	52.44	25.09
c	14.28	59.92	25.80
d	4.99	69.84	25.17

Table II. Starting Compositions and Analyses of the System $Na_5P_3O_{10}$–$Na_2B_4O_7$–H_2O

Initial Composition, Wt. %			Liquid Phase, Wt %			Wet Residue, Wt, %		
$Na_5P_3O_{10}$	$Na_2B_4O_7$	H_2O	$Na_5P_3O_{10}$	$Na_2B_4O_7$	H_2O	$Na_5P_3O_{10}$	$Na_2B_4O_7$	H_2O
17.96	1.00	81.04	. . .	. . .	86.06	. . .	. . .	. . .
16.95	2.00	81.05	. . .	. . .	84.97	. . .	. . .	. . .
13.00	8.00	79.00	13.58	1.91	84.51	14.26	20.24	65.60
10.97	9.98	79.06	12.38	1.46	86.16	4.84	29.61	65.55
9.00	11.00	80.00	11.19	1.62	87.19	7.51	27.81	64.68
9.02	11.02	79.96	10.84	1.54	87.62	1.61	35.67	62.72
5.96	18.93	75.10	8.95	1.64	89.42	0.67	43.33	56.00
6.00	8.00	86.00	7.58	1.35	91.07	3.47	31.20	65.33
3.00	7.00	90.00	3.23	2.70	94.07	1.99	29.55	68.46
1.00	8.00	91.00	1.29	3.23	95.48	1.03	33.19	65.78

to system. In the well-behaved systems, the data were reproducible to about ±0.3% per phase. For the systems $K_5P_3O_{10}$–$Na_5P_3O_{10}$ and $Na_3P_3O_9$–$Na_4P_4O_{12}$, it was difficult to obtain data with errors less than about ±0.5% per phase, exclusive of water which could always be determined to ±0.1% by the ZnO fusion method unless there was a second volatile component in the system. For the system $Na_5P_3O_{10}$–$(NH_2)_2CO$–H_2O, both water and urea were expelled by heating the ZnO samples to 1000° C. for 30 minutes. Water was calculated as the difference between the total weight loss and the weight of urea as determined by a nitrogen analysis (*8*).

If there was disagreement between the completely analyzed and the preliminary diagrams to indicate that equilibrium had not been established, a second method was employed. New samples were prepared with composition values very close to the expected liquidus. After 5 days in the thermostatically controlled bath, the liquid phase was analyzed and the quantity of solids were compared with the predicted values. The system was judged to be at equilibrium if the values agreed with the completely analyzed diagrams.

DISCUSSION

No condensed phosphate is in true equilibrium in aqueous media. The hydrolytic degradation of polyphosphates is usually decreased in basic media (*6*), while the trimeta- and tetrametaphosphates exhibit maximum stability at pH values near seven (*9*). The polyphosphates containing more than three phosphorus atoms per molecule are probably too unstable in aqueous media for them to be candidates for aqueous phase diagram studies. Relatively low temperatures must be used in the study of all polyphosphate systems. The activation energies for the degradation of polyphosphates is usually in the neighborhood of 20 to 25 kcal.

Figure 1 contains trimeta- and tetrametaphosphates, which are ring compounds. Trimetaphosphate is a six-membered ring of alternate phosphorus and oxygen atoms, while tetrametaphosphate is an eight-membered ring. At high pH values, the ring phosphates rapidly open to the chain polyphosphates, and the systems must be carefully analyzed for both poly- and metaphosphate when solubility equilibrium is not established rapidly.

Figure 2 is the phase diagram for a polyphosphate chain, $Na_4P_2O_7$, and a ring phosphate, $Na_3P_3O_9$. These two phosphates are the end members (lowest molecular weight) of the poly- and metaphosphate systems, respectively.

The system $Na_5P_3O_{10}$–$K_5P_3O_{10}$–H_2O is of interest because solid solutions are formed in the $K_5P_3O_{10}$ rich portions of the diagram. In the anhydrous system there is a double salt, $Na_5P_3O_{10} \cdot K_5P_3O_{10}$ (*10*). If one dehydrates the solid solutions of the aqueous system, the double salt is again obtained, and conversely, a solid solution is obtained by

Table III. Starting Compositions and Analyses of the Ternary Systems

Initial Composition, Wt. %			Saturated Liquor, Wt. %		
$Na_5P_3O_{10}$	Na_2SO_4	H_2O	$Na_5P_3O_{10}$	Na_2SO_4	H_2O
15.01	5.01	79.98	8.39	5.67	85.94
15.01	10.06	74.93	5.68	11.66	82.66
11.89	15.06	73.05	4.25	16.93	78.82
9.83	20.07	70.10	3.22	22.18	74.60
7.04	25.14	67.81	2.56	26.91	70.53
5.94	29.96	64.10	2.23	27.81	69.96
2.20	29.91	67.89	2.10	27.95	69.95
$Na_5P_3O_{10}$	Na_2SiO_3	H_2O	$Na_5P_3O_{10}$	Na_2SiO_3	H_2O
13.11	2.07	84.83	9.81	2.16	88.03
14.01	4.00	81.99	7.33	4.65	88.02
12.99	7.99	79.02	4.43	9.44	86.13
12.00	12.01	75.99	2.98	14.18	82.84
10.99	15.99	73.01	2.09	18.92	78.99
10.00	20.00	70.00	1.79	20.81	77.40
7.00	23.00	70.00	1.70	20.77	77.53
4.01	25.01	70.98	1.67	20.91	77.42
1.00	25.00	74.00	1.19	20.85	77.96
. . .	30.00	70.00	. . .	21.55	78.45
$Na_5P_3O_{10}$	$(NH_2)_2CO$	H_2O	$Na_5P_3O_{10}$	$(NH_2)_2CO$	H_2O
14.99	5.00	80.01	6.68	5.42	87.90
15.00	13.00	72.00	6.80	14.57	78.64
14.97	19.97	65.06	4.82	22.93	72.25
14.99	25.00	60.01	3.68	29.22	67.10
14.99	30.99	54.02	2.58	36.69	60.73
15.02	37.21	47.77	1.87		
14.99	44.99	40.02	1.21	54.36	44.43
9.98	49.99	40.02	1.17	55.23	43.60
9.99	54.90	35.11	1.15		
4.01	50.99	45.01	1.32	52.13	46.55
4.90	58.87	36.22	1.12		
0.50	59.29	40.22	0.75		

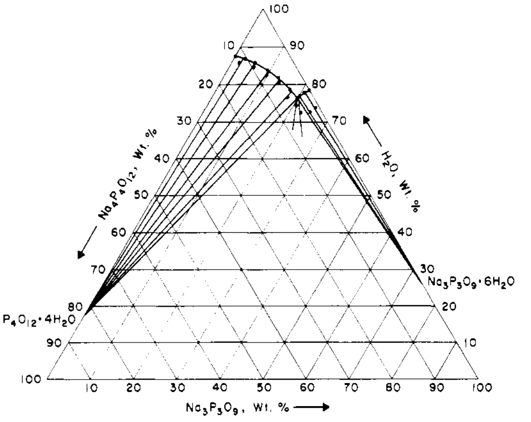

Figure 1. System $Na_4P_4O_{12}$–$Na_3P_3O_9$–H_2O at 30° C.

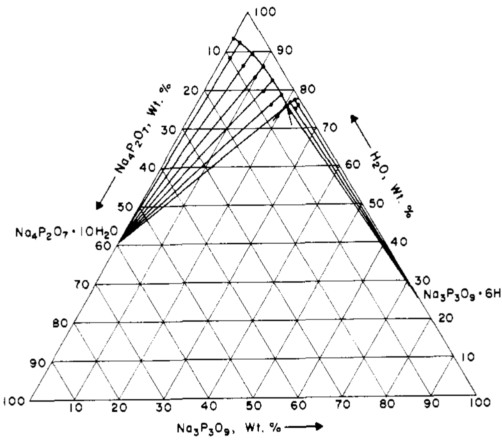

Figure 2. System $Na_4P_2O_7$–$Na_3P_3O_9$–H_2O at 30° C.

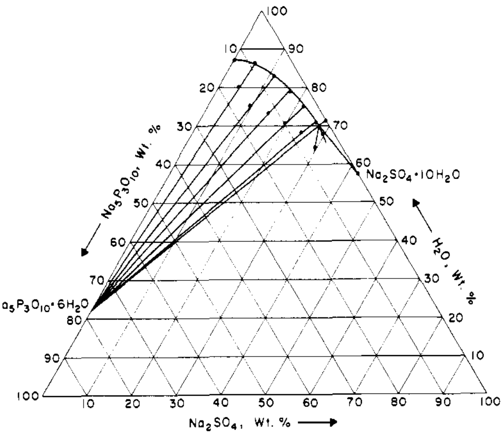

Figure 5. System $Na_5P_3O_{10}$–Na_2SO_4–H_2O at 30° C.

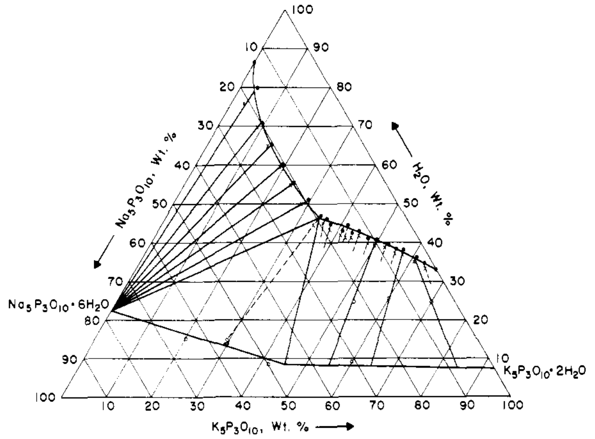

Figure 3. System $Na_5P_3O_{10}$–$K_5P_3O_{10}$–H_2O at 30° C.

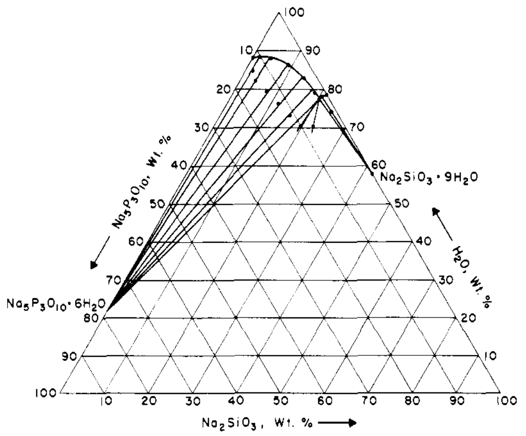

Figure 6. System $Na_5P_3O_{10}$–Na_2SiO_3–H_2O at 30° C.

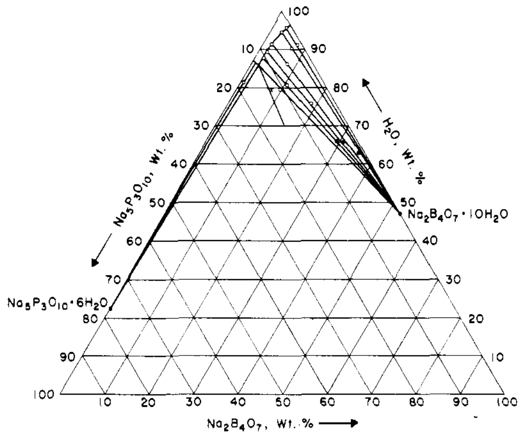

Figure 4. System $Na_5P_3O_{10}$–$Na_2B_4O_7$–H_2O at 30° C.

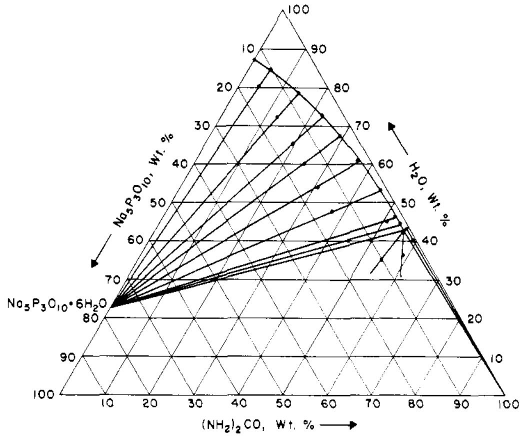

Figure 7. System $Na_5P_3O_{10}$–$(NH_2)_2CO$–H_2O at 30° C.

hydrating the double salt. The solid solutions of Figure 3 are dominated by the $K_5P_3O_{10} \cdot 2H_2O$ and the composition may be expressed as $a Na_5P_3O_{10} \cdot b K_5P_3O_{10} \cdot 2(a + b)H_2O$, where a and b are the moles of $Na_5P_3O_{10}$ and $K_5P_3O_{10}$, respectively.

Figure 4 is the phase diagram for sodium tripolyphosphate, $Na_5P_3O_{10}$ and $Na_2B_4O_7$. These compounds are often encountered in detergent systems. Figure 5 is the phase diagram for $Na_5P_3O_{10}$ and Na_2SO_4. Sodium sulfate is also a constituent of detergent systems. Figure 6 is a similar diagram containing sodium tripolyphosphate and sodium metasilicate. Figure 7 shows that urea reduces the solubility of sodium tripolyphosphate, but even in solutions saturated with urea, the sodium tripolyphosphate hexahydrate remains the stable hydrate. Of the systems studied, only $K_5P_3O_{10}$ increased the solubility of sodium tripolyphosphate in water.

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Vapor-Liquid Equilibria of the Benzene–Cyclohexane–Acetic Acid System at Atmospheric Pressure

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Vapor-liquid equilibrium data of benzene–cyclohexane–acetic acid system are determined experimentally at atmospheric pressure. The ternary system is azeotropic. The activity coefficients are correlated by Van Laar equations involving the three relevant binary constants.

THE separation of the azeotropic mixture of benzene and cyclohexane has been studied by previous workers using various third components including *n*-propanol (*5*), methyl ethyl ketone (*7*), diethyl ether (*9*), and ethyl acetate (*1*). In the present work, acetic acid is chosen as the third component. A comparative study can be made regarding the suitability of the chosen third component.

APPARATUS

The vapor-liquid equilibrium data were determined in a Fowler-Norris still (*2*) with a special heating system for better agitation. To have a decreased total capacity for each run, an equilibrium still with reduced dimensions was used. The still was standardized with the benzene-acetic acid system for which equilibrium data have been reported (*3, 6*). The temperature was measured by a set of short range thermometers (0.2° C. accuracy). Radiation correction for the exposed thread as well as the boiling point correction to 760 mm. of mercury were applied as described by Hala *et al.* (*4*). The pressure variation from 760 mm. of mercury was ± 5 mm. of mercury.

ANALYSIS

Refractive index and specific gravity at 30° C. were chosen for analysis. The measurements were made with the aid of an ultra thermostat maintained at 30° ± 0.05° C., a semimicro Mettler balance, and an Abbé refractometer provided with a source for monochromatic light. A 20-ml. pycnometer was used for specific gravity determination.

Nine binary mixtures of benzene and cyclohexane with various concentrations were prepared. Then each one was subdivided into a number of fractions when various quantities of acetic acid were added to each of these fractions. Specific gravity and refractive index were determined for each of the ternary mixtures thus prepared. The data were first plotted on linear coordinates. Then, from these graphs, constant property compositions were read, and constant specific gravity and refractive index lines were constructed (Figure 1). This was used as a standard graph for analysis.

EQUILIBRIUM DATA AND CORRELATION

The properties of the pure components are given in Table I. The equilibrium data are presented in Table II and in

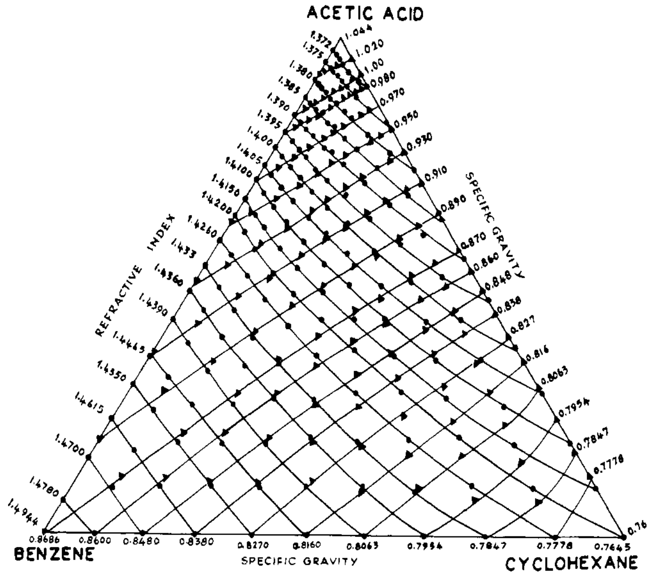

Figure 1. Standard data for analysis
▲ Constant specific gravity lines
● Constant refractive index lines