$$\Delta V^E = V^E(\text{obsd}) - V^E(\text{calcd (eq 1)})$$

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Two-Liquid-Phase Boundaries and Critical Phenomena at 275–400 °C for High-Temperature Aqueous Potassium Phosphate and Sodium Phosphate Solutions. Potential Applications for Steam Generators

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Two-liquid-phase boundaries at temperatures between 275 and 400 °C were determined for potassium phosphate and sodium phosphate aqueous solutions for compositions from 0 to 60 wt % dissolved salt. The stoichiometric mole ratios, K/PO_4 or Na/PO_4, were varied from 1.00 to 2.12 and from 1.00 to 2.16 for the potassium and sodium systems, respectively. Liquid–vapor critical temperatures were also determined for most of the dilute liquid phases that formed. The minimum temperatures (below which a single solution existed) of two-liquid-phase formation were 360 °C for the potassium system and 279 °C for the sodium system at mole ratios of 2.00 and 2.16, respectively. For the sodium system at mole ratios greater than 2.16, solids crystallized at lower temperatures as expected from earlier studies. In contrast, potassium solutions that were explored at mole ratios from 2.12 to 3.16 and at temperatures below 360 °C did not produce solid phases or liquid–liquid immiscibilities. Aside from the generally unusual observations of two immiscible liquids in an aqueous inorganic salt system, the results could possibly be applied to the use of phosphate additives in steam power generators.

Introduction

High-temperature aqueous sodium phosphate solutions of very low concentrations (0–100 ppm) have been applied to reducing scale formation in power plant steam generators as critically reviewed by Garnsey (*1*). However, in recent times a particular corrosion of steam generator tubes in nuclear pressurized water systems (the corrosion commonly defined as "thinning") was attributed in part to sodium phosphate additives. Consequently, their use in nuclear pressurized water power plants was greatly reduced, which appeared to diminish the problem of thinning. In some steam generators corrosion subsequently occurred to form oxides in the holes of support plates through which steam generator tubes passed. Continued corrosion has "dented" steam generator tubes and has even necessitated costly replacement of some of the steam generators.

After the discovery by Broadbent et al. (*2*) that aqueous solutions of disodium hydrogen phosphate form two immiscible liquids at temperatures near 300 °C, Garnsey (*1*) proposed that the resulting concentrated and strongly corrosive solution, possibly produced by boiling concentration, may have corroded the steam generator tubes to cause thinning. Recently, the analogous dipotassium hydrogen phosphate–water system has been studied at this laboratory at temperatures from 100 to 400 °C (*3*), motivated by the earlier work of Broadbent et al. (*2*), by the proposals of Garnsey (*1*), and by knowledge that at temperatures below 100 °C potassium salts are more soluble than the analogous sodium salts (*4*, *5*). This recent work showed that aqueous K_2HPO_4 solutions at high temperatures still were much more soluble than those of Na_2HPO_4. A two-liquid-phase region was also discovered but with a minimum temperature of 360 °C, which was approximately 85 °C higher than that estimated for corresponding Na_2HPO_4 solutions (*2*). Substitution of potassium phosphate for sodium phosphate as an additive would therefore prevent the formation of a second liquid phase in the region of steam generator operation (275–325 °C) that otherwise could have caused thinning as proposed by Garnsey (*1*). This substitution might again make phosphates useful in eliminating particular problems of corrosion (including denting) as suggested earlier (*3*).

The present study on liquid–liquid immiscibilities expands upon those presented previously by Broadbent et al. (*2*), very recently by Wetton (*6*), and by Marshall et al. (*3*) to quantitatively describe comparative temperature–composition immiscibility boundaries for aqueous sodium phosphate and potassium phosphate solutions of mole ratios, Na/PO_4 and K/PO_4, varying from 1.0 to just above 2.0. The two systems are explored at higher mole ratios and show the expected formation of solid phases for the sodium system (*6*–*10*) but none for the potassium system over the range of exploration.

Experimental Procedures

Reagents. Dipotassium hydrogen phosphate (K_2HPO_4) and tripotassium phosphate hydrate ($K_3PO_4 \cdot nH_2O$) used were J. T. Baker Chemical Co. analyzed reagent grade, and potassium dihydrogen phosphate (KH_2PO_4) was Fisher Scientific Co. certified ACS grade. Disodium hydrogen phosphate (Na_2HPO_4) and trisodium phosphate hydrate (analyzed to be $Na_{3.16}(OH)_{0.16}PO_4 \cdot 12H_2O$) were obtained from Fisher Scientific Co., and sodium dihydrogen phosphate hydrate ($NaH_2PO_4 \cdot H_2O$) was obtained from J. T. Baker Co.; these salts were the same grades of purity as those for the potassium phosphates.

Liquid–Liquid Immiscibility. Several series of solutions, each of a given constant mole ratio, K/PO_4 or $NaPO_4$, but with differing weight percents for each solution, were prepared gravimetrically from the above solids and distilled water. Some compositions with high weight percent solid were not entirely soluble at 25 °C, as expected from the literature (*4*, *5*). These particular compositions were heated at 50–75 °C in order to

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fully dissolve the solids. Upon being recooled to 25 °C, some of these solution mixtures (containing either potassium or sodium) rather quickly recrystallized, in contrast to the observed metastable behavior of concentrated K_2HPO_4–H_2O solutions (*3*). Consequently, the filling of capillary tubes with the concentrated solutions, for using the synthetic method, needed to be performed rapidly with warmed tubes. The synthetic method, by which solutions of known compositions are sealed in glass tubes and the temperature at which a phase change occurs is recorded, was used for the present study. The procedure and the phase-study apparatus (*11*) were described in the previous work (*3*). Fused silica capillary tubes were used for containing the solutions.

For several experiments with highly alkaline solutions of mole ratios, K/PO_4 or Na/PO_4, greater than 2.2, a semiclear Teflon (tetrafluoropolyethylene) tube liner was inserted into a 25-cm long fused silica tube of 2-mm inner diameter. A solution of sufficient volume to nearly fill the tube at high temperatures was sealed within the silica tube. This tube was inserted into the phase-study apparatus, with the ends projecting out for coolness, and the phase behavior of the solution (protected by the Teflon liner from silica dissolution) was observed at temperatures up to 310 °C.

A chromel–alumel thermocouple together with a digital-readout unit (Doric 412A; Emerson Electric Co.) was used for temperature measurement. The thermocouple was calibrated to 0.1 °C over the range from 0 to 400 °C. When the thermocouple was positioned in the apparatus, many separate experimental determinations of the liquid–vapor critical temperature of pure water gave the accepted value of 374.2 °C (*12*) to a precision of ±0.1 °C. This temperature was redetermined periodically during the measurements for assurance of accurate readings.

The temperatures at which a second liquid phase formed (or disappeared) were obtained by observing the phase change with both slowly increasing and decreasing temperatures. The precision in determination of each value is included in the tables. Both the precision and the accuracy of measurement may differ for each composition generally because of (a) the different volume ratios of the two liquids upon appearance of immiscibility, (b) some small amount of reaction (a very large amount at mole ratios greater than 2.2) with the fused silica containment tube interfering with the observations, and (c) at the highest temperatures some concentration of the liquid phases due to loss of water to the vapor phase. Generally, the tubes were approximately $^1/_2$ to $^1/_3$ full upon appearance of immiscibility. With these considerations, the accuracy of each value probably is less than the precision but may be within 0.5–1.0 °C.

Liquid–Vapor Critical Phenomena. Liquid–vapor critical temperatures for the dilute liquid phases (that is, the temperature at which the vapor phase becomes identical with the dilute liquid phase, and therefore the meniscus between these two phases disappears with rising temperature) were determined similarly with both increasing and decreasing temperature. Since the true critical temperature (t_c) is obtained only when the dilute liquid phase (L_1; for these experiments) approaches exactly the same volume as the vapor at the critical temperature (*13*, *14*), the results obtained generally may not be as accurate (but probably within 1.0–1.5 °C) as those for immiscibility. Precisions of measurement are included in the tables, with the best precisions obtained (±0.1–0.2 °C) for those experiments for which the L_1 to vapor volume ratio appeared to be very close to unity and the temperatures of disappearance (or appearance) of the meniscus were very sharp. These values should be also the most accurate.

Results and Discussion

General Results. Tables I and II give the experimentally obtained values for the potassium phosphate and sodium phosphate systems, respectively, for boundary limits of liquid–liquid immiscibility. Values derived from plots shown in previous studies (*2*, *6*, *8*, *9*) are given also. Liquid–vapor critical temperatures are included for most of the dilute liquid phases that formed at lower temperatures. The solutions prepared were of mole ratios, K/PO_4 or Na/PO_4, of 1.0, 1.2, 1.5, 2.0, 2.12 (for K), and 2.16 (for Na). For a given series of solutions of constant mole ratio but of differing weight percents, immiscibility was not observed for some of the solutions of highest weight percent. As indicated in Tables I and II, these solutions were taken to a temperature of 410 °C. At this temperature, the concentrated liquid phase remained a clear liquid of moderately high fluidity. Since the dilute liquid never formed at lower temperatures, there was no critical temperature to be observed.

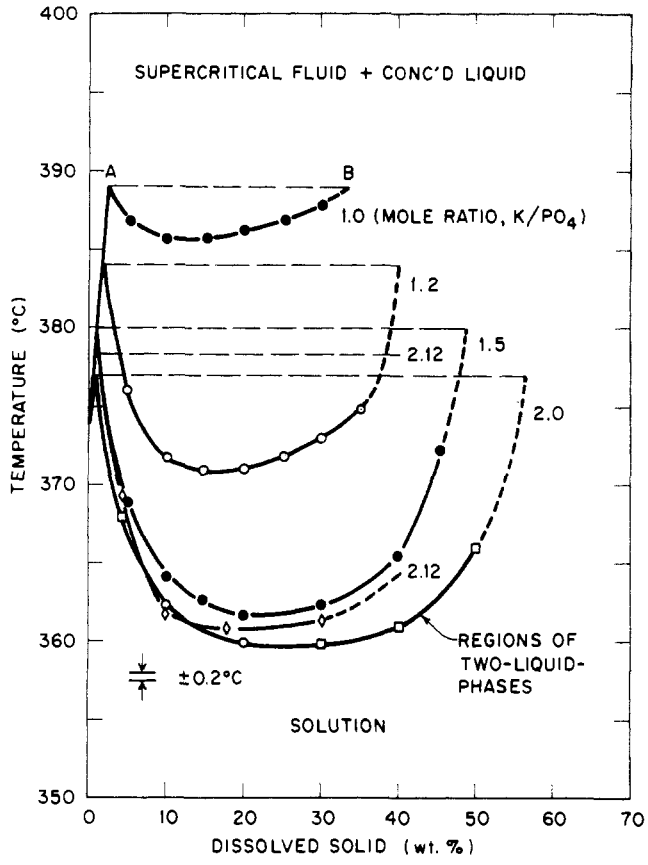

Figure 1. Two-liquid-phase regions for aqueous solution mixtures of potassium phosphates for mole ratios, K/PO_4, from 1.00 to 2.12: (O, ●, ◊) present study; (□) Marshall et al. (*3*).

Potassium Phosphate Aqueous Phase Behavior. Figure 1 shows the plots of boundary temperatures of two-liquid-phase formation for aqueous solutions of potassium phosphates for the several constant mole ratios, K/PO_4, as given in Table I and reported earlier for K_2HPO_4–H_2O (*3*). Two points at 20 and 30 wt % K_2HPO_4 were rerun in this work (Table I), and these have been substituted for the earlier values (*3*), the temperatures for which appeared to have been reversed. The temperature scale is greatly expanded and shows the extent of excellent correlation of individual measurements with each other (±0.25 °C).

The determined critical temperatures for each series of solutions of a constant mole ratio, K/PO_4, represent the approximate critical temperature for the dilute liquid at a composition estimated by extrapolating the immiscibility curve upward to the reported values of t_c. Thus, after formation of the two liquid phases, the dilute phase becomes more dilute with rising temperature, finally reaching an estimated composition (at A in Figure 1 for a mole ratio of 1.0) where the critical phenomenon (for this phase) is observed. Conversely, the concentrated liquid becomes more concentrated with rising temperature, and re-

Table I. Aqueous Potassium Phosphate Solutions of Mole Ratios, K/PO_4, from 1.00 to 2.12, Temperatures of Appearance (with Rising Temperature) of Second Liquid Phases, and Liquid-Vapor Critical Phenomena (for the Dilute Liquid Phases)

		immiscibility boundary		critical phenomenon	
solute stoichiometry	solute wt %[a]	t,[b] °C	phase appearing[c]	t, °C	est wt % solute[d]
KH_2PO_4 (K/PO_4 = 1.00)	5.05	386.8 ± 0.2	L_2	389.0 ± 0.5	2.2
	10.09	385.6 ± 0.1	L_2	388.5 ± 0.5	2.2
	14.8	385.7 ± 0.1	L_2	389.0 ± 0.5	2.2
	20.0	386.1 ± 0.2	L_*	388.9 ± 0.2	2.2
	25.0	386.9 ± 0.4	L_1	388.7 ± 0.5	2.2
	29.5	387.8 ± 0.4	L_1	389.0 ± 0.5	2.2
	33[d]	389[d]	L_1	389[d]	2.2
	41.5	e	e	e	e
$K_{1.2}H_{1.8}PO_4$ (K/PO_4 = 1.20)	5.07	376.0 ± 0.3	L_2	384.0 ± 0.5	1.8
	10.3	371.8 ± 0.2	L_2	383.9 ± 0.3	1.8
	15.1	371.0 ± 0.1	L_2	384.9 ± 0.2	1.8
	20.2	370.9 ± 0.2	L_2	384.0 ± 0.5	1.8
	25.1	372.0 ± 0.2	L_*	385.0 ± 0.2	1.8
	30.2	373.0 ± 0.1	L_1	384.5 ± 0.5	1.8
	35.1	374.9 ± 0.1	L_1	385.1 ± 0.1	1.8
	39[d]	384.5[d]	L_1	384.5[d]	1.8
	40.2	e	e	e	e
	50.1	e	e	e	e
$K_{1.5}H_{1.5}PO_4$ (K/PO_4 = 1.50)	5.02	369.0 ± 2.0	L_2	380.1 ± 0.1	1.5
	10.05	364.0 ± 1.0	L_2	380.0 ± 0.5	1.5
	15.1	362.7 ± 0.1	L_2	380.0 ± 0.5	1.5
	20.1	361.7 ± 0.1	L_2	380.0 ± 0.5	1.5
	30.2	362.5 ± 0.1	L_*	380.0 ± 0.5	1.5
	39.8	365.0 ± 0.5	L_1	380.5 ± 0.5	1.5
	45.2	372.5 0.5	L_1	380.0 ± 0.2	1.5
	49[d]	380[d]	L_1	380[d]	1.5
	50.3	e	e	e	e
K_2HPO_4[f] (K/PO_4 = 2.00)	10.3	362.4 ± 0.4	L_2	375.9 ± 0.2	1
	20.0	360.0 ± 0.2	L_2	376.8 ± 0.5	1
	56[d]	377[d]	L_1	377[d]	1
$K_{2.12}H_{0.88}PO_4$ (K/PO_4 = 2.12)	4.73	369.4 ± 0.2	L_2	377.3 ± 0.2	2
	9.88	361.4 ± 0.5	L_2	378.0 ± 0.2	2
	16.7	360.9 ± 0.2	L_2	379.2 ± 0.4	2
	30.3	362.1 ± 0.2	L_2	378.5 ± 0.4	2

[a] Wt % dissolved solid as written. [b] Lower boundary of observation (appearance of second liquid phase with rising temperature). [c] L_1 = dilute liquid phase; L_2 = concentrated liquid phase; L_* = liquid phase near the consolute solution composition (where composition L_1 equals composition L_2). [d] Estimated from plots of Figure 1; values at upper temperature limit of immiscibility. [e] No second liquid or critical phenomenon is observed at temperatures up to 410 °C. [f] Additional values given by Marshall et al. (ref 3).

mains a liquid at least up to a temperature of 410 °C (Table I). Above the critical temperature of the dilute phase, the composition of concentrated phase depends upon the relative volume of supercritical fluid, which may be varied by changing the pressure on the system.

Three-Component Nature of the System. The several immiscibility phase boundaries shown in Figure 1 in reality represent slices at several constant mole ratios, K/PO_4, in a three-dimensional figure for the full three-component condensed system K_2O–P_2O_5–H_2O. The portions shown can be described by a subsystem KH_2PO_4–K_3PO_4–H_2O. For compositions near that at the consolute solution point (CSP, the point of disappearance of immiscibility at which the compositions of both phases become identical), it was difficult to detect which phase (the dilute or concentrated) appeared first with rising temperature. Table I thus gives the phases appearing (L_1 or L_2), but for those in the vicinity of the CSP the symbol L_* is used to indicate this uncertainty. The CSP for each curve in Figure 1 appears to be at a slightly higher temperature than the minimum temperature of immiscibility. For these plots (or slices), a three-component system would not require the CSP to be at the minimum temperature. A temperature at the CSP higher than the minimum even substantiates the necessity for full description by three or more components (*15*).

It therefore follows for a three-component system that the boundary curves shown in Figure 1 cannot be used to obtain an exact composition of the second liquid phase that appears with rising temperature. With a two-component system, the compositions in equilibrium are given at the two intersections of a horizontal tie line (at a constant temperature) with a boundary curve. For the present system it may appear that the boundaries shown approximate behavior as separate two-component systems. For example, all critical temperatures for the dilute phases from different solution compositions of a given mole ratio, K/PO_4, are nearly the same (Table I). This observation suggests that each slice can be treated approximately as a two-component system, with the composition of the concentrated phase at the upper two-liquid-phase limit (for a mole ratio of 1.0) being close to that at point B in Figure 1.

Immiscibility Behavior at K/PO_4 Ratios above 2.12. It is of much interest to know the phase behavior of potassium phosphate solutions of mole ratio, K/PO_4, greater than 2.12. Presently, the very large reactivity of the fused silica tubes used in the experiments toward these solutions of high alkalinity has precluded the attainment of reliable measurements.

In Figure 2 (part A) is plotted the minimum temperature of immiscibility for the several series of curves (Figure 1) against the mole ratio, K/PO_4, for each series. We observe an initially rapid decrease in temperature of immiscibility with increasing K/PO_4 ratio, which reaches zero change at the composition, K_2HPO_4, and then increases with a further increase in ratio. The solid, KOH, is highly soluble in water solution at low temperatures, and at high temperatures no liquid–liquid immiscibility or retrograde solubility for KOH solutions is expected. With the minimum temperature of immiscibility reached for K_2HPO_4–H_2O solutions, it would appear that increasing the mole ratio, K/PO_4,

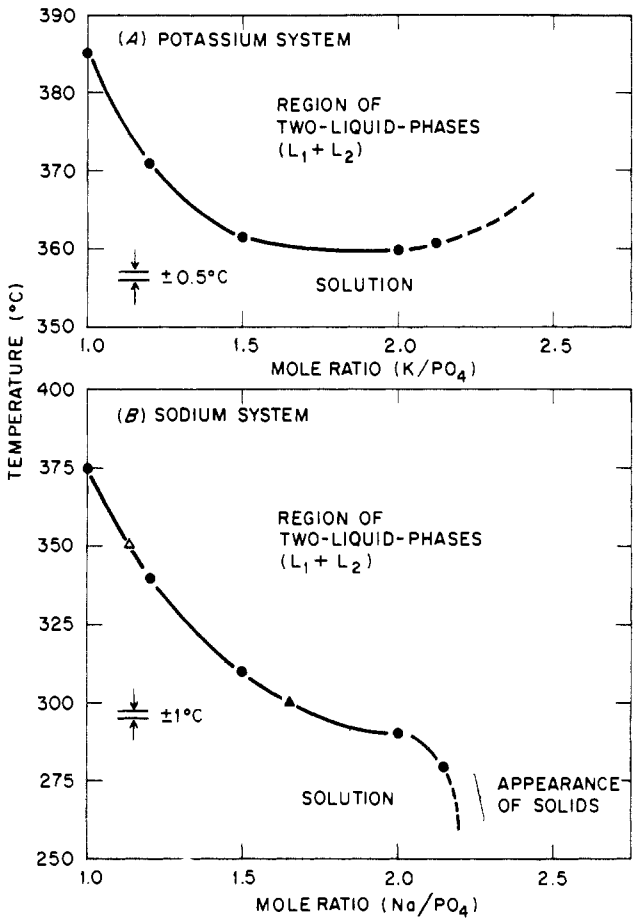

Figure 2. Lower limits of two-liquid-phase formation for aqueous solution mixtures of mole ratios, K/PO_4 (part A) and Na/PO_4 (part B), from 1.00 to above 2.00: (●) present study; (△, 350 °C) Wetton (*6*); (▲, 300 °C) Broadbent et al. (*2*).

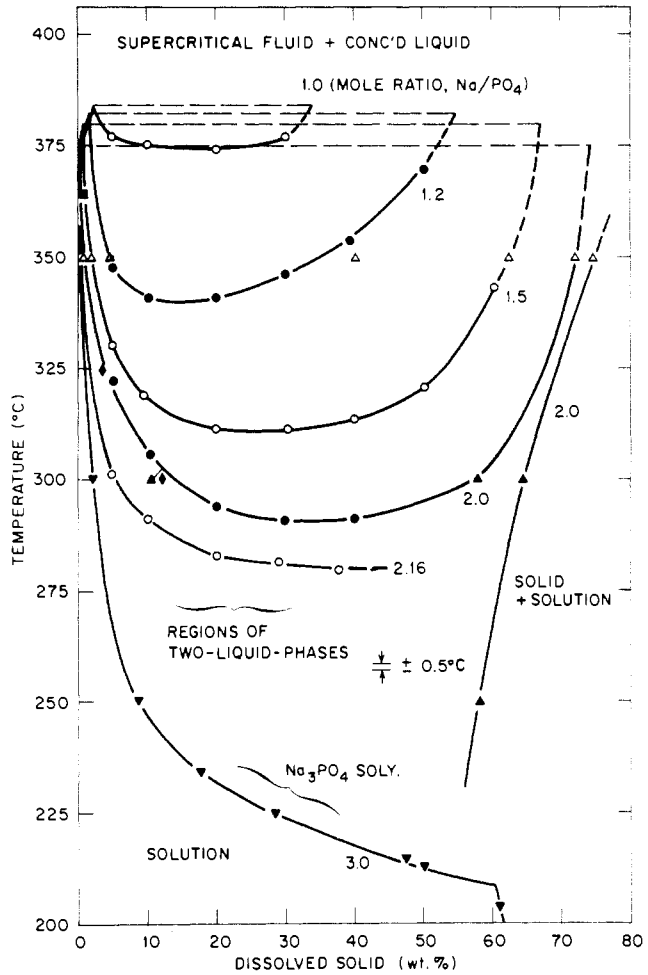

Figure 3. Two-liquid-phase and solution–solid boundaries for aqueous solution mixtures of sodium phosphate salts of mole ratios, Na/PO_4, from 1.00 to 3.00 at 200–400 °C: (○, ●) present study; (△, 350 °C) Wetton (*6*); (▲, 250 and 300 °C) Broadbent et al. (*2*); (♦, 300 and 324 °C) Panson et al. (*9*); (■, 365 °C) Ravich and Shcherbakova (*8*); (▼, 200–350 °C) Schroeder et al. (*7*).

from 2.0 toward 3.0 and even toward infinity (that is, for KOH–H_2O) will simply increase the immiscibility temperature or eliminate immiscibility entirely. This behavior is estimated by the extrapolated dashed line in Figure 2 (part A).

Reactions with Silica at High K/PO_4 Ratios. As expected, potassium phosphate (and also sodium phosphate) solutions showed increasing reaction rates with silica containment tubes as the mole ratio, K/PO_4, was increased from 2.0 to 3.16. Immiscibility and critical temperatures for solutions of mole ratio 2.12 were obtained because of the relatively short times (3–5 min) at high temperatures. For higher ratios, even these times were too long to avoid very rapid dissolution of silica and consequent production of gellike solids that formed at 225–300 °C; in many solutions of high concentrations these gels even appeared first as second liquid phases. The question arose whether the dissolved silica produced the gels. Several experiments were thus performed on K_3PO_4 solutions sealed in Teflon-lined tubes (Experimental Procedures) and held at temperatures up to 310 °C for 1–2 h and in gold-electroplated vessels (*3*) at 300–350 °C for 3–4 h. In contrast to the rapid gel formation in unlined tubes, these solutions remained clear; solids were not formed. Rapid reaction with silica may have produced second liquid phases (converting to gellike solids upon further reaction) similar to those observed for the system Na_2O–SiO_2–H_2O at 250–350 °C (*16*). The dissolution rate appeared to slow down as potassium silicate solids were produced and the remaining dissolved salt stoichiometry approached that of K_2HPO_4. For example, experiments in unlined silica tubes with solutions of mole ratio 2.5 and 3.16 that produced solid at 225–300 °C gave immiscibility temperatures for the remaining solution phase within 1 °C of those for K_2HPO_4 solutions reported in Table I.

Sodium Phosphate Aqueous Phase Behavior. Figure 3 shows the experimentally determined values for liquid–liquid immiscibility and the estimated compositions and liquid–vapor critical temperatures for dilute liquid phases for the several series of solution compositions of constant mole ratios, Na/PO_4, as given in Table II. Also shown are values of liquid–liquid immiscibility reported by Broadbent et al. (*2*) in their discovery of immiscibility in aqueous solutions of Na_2HPO_4 and some interpolated values from the very recent work Wetton (*6*), from Panson et al. (*9*), and from Ravich and Shcherbakova (*8*). Values of all investigations were obtained by direct sampling and analysis of the phases and also by a visual method by Broadbent et al. and Wetton. Agreement of the present measurements with these values appears to be excellent.

The interpretations for the immiscibility boundaries of the sodium phosphate solutions are the same as those given above for potassium phosphate solutions. The only differences in behavior are the temperatures of immiscibility, the behavior at ratios above 2.0, and the much wider spread of temperature for the mole ratios, Na/PO_4, changing from 1.0 to 2.16. Thus, it should be emphasized that, although the comparative weight percent scale is the same for Figures 1 and 3, the temperature scale is 3 times expanded in Figure 1.

Immiscibility and Solid–Liquid Behavior at Na/PO_4 Ratios Greater than 2.0. Figure 2 (part B) shows the minimum temperatures of immiscibility for the several series of sodium

Table II. Aqueous Sodium Phosphate Solutions of Mole Ratios, Na/PO_4, from 1.00 to 2.16, Temperatures of Appearance (with Rising Temperature) of Second Liquid Phases, and Liquid-Vapor Critical Phenomena (for the Dilute Liquid Phases)

		immiscibility boundary		critical phenomenon	
solute stoichiometry	solute wt %[a]	t,[b] °C	phase appearing[c]	t, °C	est wt % solid[d]
NaH_2PO_4 (Na/PO_4 = 1.00)	4.96	376.6 ± 0.2	L_2	383.4 ± 0.4	2.5
	9.98	375.0 ± 0.5	L_2	383.7 ± 0.2	2.5
	20.0	374.0 ± 0.2	L_*	383.5 ± 0.2	2.5
	30.1	376.5 ± 0.3	L_1	384.6 ± 0.3	2.5
	34[d]	384[d]	L_1	384[d]	2.5
	40.0	e	e	e	e
	50.0	e	e	e	e
	60.1	e	e	e	e
$Na_{1.2}H_{1.8}PO_4$ (Na/PO_4 = 1.20)	4.55[f]	350[f]	L_2		2
	5.13	347.7 ± 0.5	L_2	378.4 ± 0.5	2
	10.0	340.3 ± 0.4	L_2	380.9 ± 0.5	2
	20.1	340.7 ± 0.3	L_2	382.9 ± 0.5	2
	30.3	345.7 ± 0.1	L_*	383.5 ± 0.6	2
	39.8	353.5 ± 0.1	L_1	380 ± 2	2
	40.6[f]	350[f]	L_1		2
	50.3	369.0 ± 0.5	L_1	380 ± 2	2
	55[d]	382[d]	L_1	382[d]	2
	60.1	e	e	e	e
$Na_{1.5}H_{1.5}PO_4$ (Na/PO_4 = 1.50)	2.05[f]	350[f]	L_2		1
	4.99	329.9 ± 0.1	L_2	378.4 ± 0.1	1
	9.59	319.0 ± 0.1	L_2	378.8 ± 0.1	1
	20.0	310.3 ± 0.1	L_2	379.3 ± 0.2	1
	30.3	310.1 ± 0.1	L_2	378.8 ± 0.1	1
	40.1	313.1 ± 0.1	L_*	379.3 ± 0.1	1
	50.2	319.9 ± 0.1	L_1	379.3 ± 0.1	1
	60.2	343.2 ± 0.3	L_1		1
	63.1[f]	350[f]	L_1		1
	67[d]	379[d]	L_1	379[d]	1
Na_2HPO_4 (Na/PO_4 = 2.00)	0.8[g]	365[g]	L_2		0.5
	1.14[f]	350[f]	L_2		0.5
	3.0[h]	324[h]	L_2		0.5
	5.0	321.3 ± 0.4	L_2	374.7 ± 0.5	0.5
	10.0[i]	300[i]	L_2		0.5
	10.3	305.2 ± 0.1	L_2	374.7 ± 0.5	0.5
	12.4[h]	300[h]	L_2		0.5
	20.0	293.6 ± 0.2	L_2	375.4 ± 0.5	0.5
	30.0	290.6 ± 0.2	L_2	375.1 ± 0.3	0.5
	40.0	290.6 ± 0.4	L_*	374.7 ± 0.5	0.5
	57.3[i]	300[i]	L_1		0.5
	72[f]	350[f]	L_1		0.5
	74[d]	375[d]	L_1	375[d]	0.5
$Na_{2.16}H_{0.84}PO_4$ (Na/PO_4 = 2.16)	4.85	301 ± 1	L_2		
	10.0	291 ± 1	L_2		
	20.0	282 ± 1	L_2		
	28.9	281 ± 1	L_2		
	37.5	279 ± 1	L_2		

[a] Wt % of solid as written. [b] Lower boundary of observation (appearance of second liquid phase with rising temperature). [c] L_1 = dilute liquid phase; L_2 = concentrated liquid phase; L_* = liquid phase near the consolute solution composition (where composition L_1 equals composition L_2). [d] Estimated from plots of Figure 3; values at upper temperature limit of immiscibility. [e] No second liquid or critical phenomenon is observed at temperatures up to 410 °C. [f] From plots of Wetton (ref 6). [g] From plot of Ravich and Shcherbakova (ref 8). [h] From plots of Panson et al. (ref 9). [i] From plots of Broadbent et al. (ref 2).

phosphate solutions of constant mole ratios, Na/PO_4, plotted against mole ratio. The plot is similar to that for potassium phosphate solutions (part A) up to a ratio of 2.0. As the ratio increases to 2.0 (the composition, Na_2HPO_4), the decrease in temperature with increasing ratio approaches zero but then decreases again as the ratio increases to 2.16, which essentially is at the limit of immiscibility (*2*, *6*). At mole ratios above 2.16, sodium phosphate solids are the equilibrium phases and show progressively lower solubilities at temperatures increasing above 200 °C. Earlier excellent studies describe these relations (*2*, *6–10*). A portion of the solubility curve for Na_3PO_4 obtained by Schroeder et al. (*7*) is shown in Figure 3. Solubility behavior for ratios between 2.16 and 3.00 may be estimated from this figure or from the previous studies. In order to observe the formation of solids, several solutions of mole ratios 2.5 and 3.0 were sealed in Teflon-lined silica tubes (Experimental Procedures) and in gold-electroplated vessels (*3*) and were run at temperatures between 225 and 300 °C for 3–4 h. In contrast to the clear solutions remaining after similar experiments for the potassium system at even higher temperatures, solids formed extensively in both the Teflon liners and the gold-electroplated vessels.

Comparative Immiscibility Behavior of Aqueous Potassium Phosphate and Sodium Phosphate Solutions. Figure 4 compares the temperature–composition immiscibility boundary for K_2HPO_4–H_2O with that for Na_2HPO_4–H_2O solutions. The solution–solid phase boundaries reported earlier for the two systems are shown also (*2*, *3*, *6*). The minimum immiscibility temperatures are 360 and 290 °C for K_2HPO_4 and Na_2HPO_4 solutions, respectively, or a temperature of 70 °C higher for K_2HPO_4 solutions. The compositional boundaries for saturation with a solid phase are markedly higher for K_2HPO_4 than for Na_2HPO_4 solutions.

It is interesting to note that the immiscibility points shown in

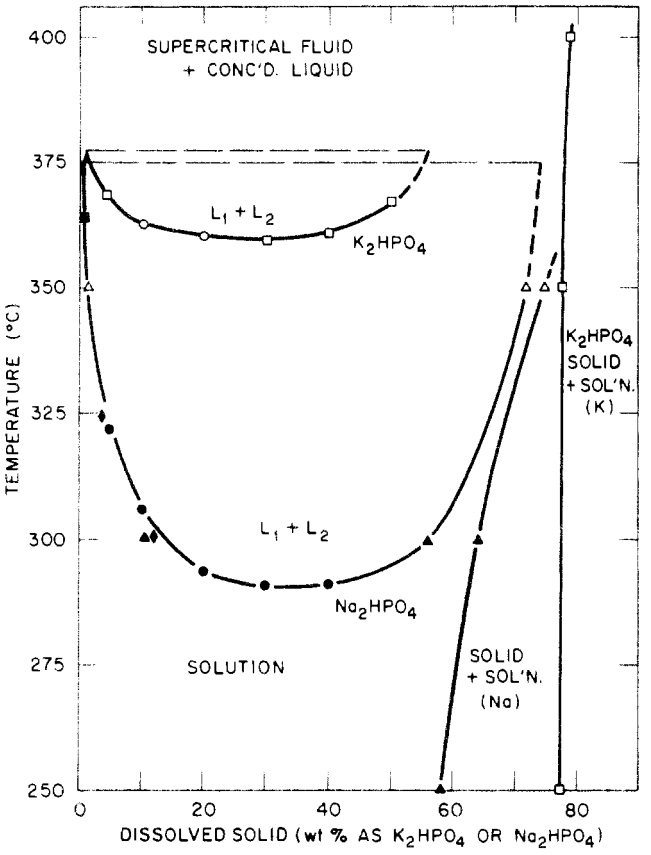

Figure 4. Comparative two-liquid-phase and solution–solid boundaries for aqueous solutions of Na_2HPO_4 and K_2HPO_4, 250–400 °C: (O, ●) present study; (□) Marshall et al. (*3*); (△, 350 °C) Wetton (*6*); (▲, 250 and 300 °C) Broadbent et al. (*2*); (♦, 300 and 324 °C) Panson et al. (*9*); (■, 365 °C) Ravich and Shcherbakova (*8*).

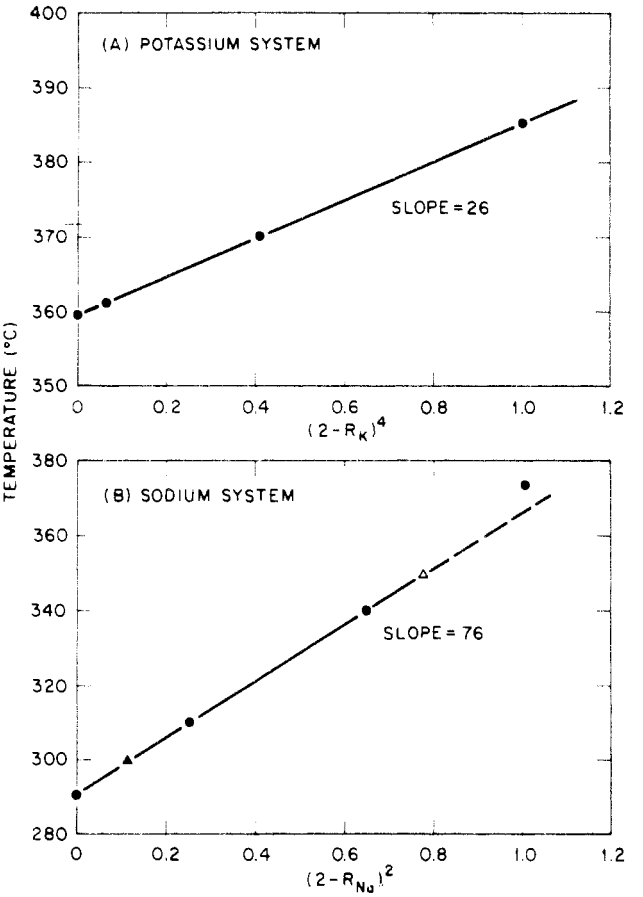

Figure 5. Lower limits of liquid–liquid immiscibility for aqueous potassium phosphate (part A) and sodium phosphate (part B) solutions plotted against $(2 - R)^n$. R = mole ratio, K/PO_4 or Na/PO_4, and n = 4 and 2 for potassium and sodium systems, respectively; (●) present study; (△) Wetton (*6*); (▲) Broadbent et al. (*2*).

Figure 2 (parts A and B) for mole ratios for 1.0 to 2.0 may easily be fitted to the equation

$$t_I = a + b(2.00 - R)^n \quad (1)$$

where t_I is the immiscibility temperature (°C), R is the mole ratio (K/PO_4 or Na/PO_4), and a, b, and n are constants. Figure 5 compares plots of t_I vs. $(2.00 - R)^n$ where the values for n are 4.00 for the potassium system (part A) and 2.00 for the sodium system (part B). Thus, the temperatures of minimum immiscibility for the aqueous potassium phosphates depend upon the fourth power of $(2.00 - R)$, and those for sodium upon the second power. This behavior appears to be striking not only because of the exactness of the values for n but also because of the exact factor of 2.00 for n between the two systems. Moreover, the slopes (Figure 5) differ almost exactly by a factor of 3.0. Perhaps part of the behavior may be speculatively related to differences in the solution species in the two systems.

Conclusions

In this study comparative immiscibility boundaries and liquid–vapor critical temperatures are presented for aqueous potassium phosphate and sodium phosphate solutions of mole ratio, alkali metal/phosphate, varying from 1.0 to 2.12 and 2.16, respectively, and at temperatures between 275 and 400 °C. Potassium phosphate solutions show higher solubilities and higher temperatures of phase homogeneity than do comparable sodium phosphate solutions. Aside from the strongly fundamental interest in the phenomenon of liquid–liquid immiscibility in aqueous–inorganic systems at high temperatures, the potential application to problems of steam power generation discussed in the Introduction should be considered.

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