Phase Equilibria in Aqueous Sodium Phosphate Solutions at Elevated Temperatures

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Solubility and phase studies for the system $Na_2O-P_2O_5-H_2O$ have been carried out at 251 and 300 °C and at the vapour pressures of the solutions. The experiments have been largely confined to the region of composition between the mol ratio $Na_2O : P_2O_5 = 1.8$ and 10.0. At both temperatures, the more alkaline saturated solutions are in equilibrium with a solid phase, $11Na_2O{\cdot}4P_2O_5{\cdot}3H_2O$, a complex orthophosphate. The less alkaline saturated solutions are in equilibrium with $Na_2[HPO_4]$ at 251 °C, and with $Na_4[P_2O_7]$ at 300 °C. However, at the higher temperature, a region of liquid–liquid immiscibility also exists.

ALTHOUGH sodium phosphates have been used in boiler-water treatment for many years, there is a scarcity of experimental data on their solubility in water at the temperatures which aqueous solutions may attain in the boilers of modern power stations (250—350 °C).

The system $Na_2O-P_2O_5-H_2O$ has been studied extensively up to 100 °C, the work of Wendrow and Kobe [1] being the most comprehensive. This covered almost the complete range of composition, and a large number of hydrates and double salts crystallising under these conditions were identified. Phase equilibria in aqueous systems with $Na_2O : P_2O_5 = 1 : 1$ have been investigated by Morey [2] up to 620 °C, but work above 100 °C has mainly been concentrated on the more alkaline compositions relevant in boiler-water treatment. Schroeder *et al.*[3] measured the solubility of trisodium phosphate up to 350 °C. However, their conclusion that anhydrous $Na_3[PO_4]$ is the equilibrium solid phase from 215 to 350 °C is not confirmed by the later work of Ravich and Shcherbakova [4] at 250—365 °C over a wider range of alkalinity. Recently, an even wider range of alkalinity was covered by Panson *et al.*[5] at 275—324 °C, but the phase equilibria in this region are still not clearly established.

In this work, we report measurements of the compositions of saturated alkaline sodium phosphate solutions and the phases in equilibrium with these solutions at two temperatures, 251 and 300 °C. This covers a wider region of composition than any previous work in this temperature range and is designed to include most of the sodium phosphate solutions likely to be produced at concentration sites [6] in boilers.

EXPERIMENTAL

Apparatus and Techniques.—The furnace was made from a cylindrical block of aluminium alloy, fitted with electric heaters and mounted so that it could be rocked about a horizontal axis. Eight autoclaves could be accommodated inside the block. A very similar system was described by Marshall and Gill.[7] All the autoclaves, filters, valves, and tubing were constructed of stainless steel, type 316, unless stated otherwise. Temperatures were monitored with chromel–alumel thermocouples connected to a Comark 'Electronic Thermometer' and could be controlled to ±0.1 °C. The overall accuracy of the measuring system was considered to be ±0.5 °C after calibration at the freezing points of Sn and Pb.

The majority of the results with the most dilute and alkaline saturated solutions were obtained using Monel alloy (Ni, 65; Cu, 30; Fe, 3%) autoclaves of 95-cm^3 internal volume. These ultimately became difficult to seal and were appreciably corroded by the more alkaline solutions, so they were replaced by pressure vessels of 73-cm^3 capacity made from Incoloy 825 (major constituents: Ni, 42; Cr, 21.5; Fe, *ca.* 30%). No significant differences in results between the two types of autoclave were observed for the less alkaline solutions.

It was usually possible to sample the saturated solutions through cooled lengths of 0.6-mm bore capillary tubing connected to the autoclaves and terminated by valves outside the furnace. Approximately 0.2 g of liquid was taken for analysis and not more than 5 g of solution was withdrawn in all. This method was not practicable for solutions whose compositions lay above the 60 °C solubility isotherm.[1] Such solutions were obtained by using nitrogen pressure to force them from the Incoloy autoclave through a filter and into a 10-cm^3 capacity autoclave. Both vessels and the interconnecting pipework were maintained at the working temperature during this operation, after which they were removed from the furnace and cooled to room temperature in *ca.* 15 min. The smaller autoclave had been weighed initially. It was reweighed at the end of the experiment and the contents, occupying 50—100% of its volume, were washed out into a graduated flask. In both techniques, the autoclaves were initially half filled with the sodium phosphate mixture. Appreciable corrosion was observed unless the air space was either evacuated or flushed with nitrogen.

Solids in equilibrium with the saturated solutions were isolated in independent experiments. The sodium phosphate mixture was held in an autoclave of *ca.* 10-cm^3 capacity fitted with a liner of poly(tetrafluoroethylene). When equilibrium had been reached, the solution could be rapidly expelled to the atmosphere, any solid being retained by a filter. The autoclave was cooled to room temperature in *ca.* 5 min, and was so designed that the solid could easily be removed for analysis. Trials in which the liquid phase was sampled and analysed gave identical results, within experimental error, to the experiments in the larger autoclaves.

Materials and Methods of Analysis.—Chemicals used were of AnalaR quality. Deionised water with a sodium concentration less than 2×10^{-7} mol dm^{-3} was used in preparing

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[1] B. Wendrow and K. A. Kobe, *Ind. and Eng. Chem.*, 1952, **44**, 1439.

[2] G. W. Morey, *J. Amer. Chem. Soc.*, 1953, **75**, 5794.

[3] W. C. Schroeder, A. A. Berk, and A. Gabriel, *J. Amer. Chem. Soc.*, 1937, **59**, 1783.

[4] M. I. Ravich and L. G. Shcherbakova, *Izvest. Akad. Nauk S.S.S.R., Sekt. Fiz-Khim. Anal.*, 1955, **26**, 348.

[5] A. J. Panson, G. Economy, C. Liu, T. S. Bulischeck, and W. T. Lindsay, jun., *J. Electrochem. Soc.*, 1975, **122**, 915.

[6] G. M. W. Mann, *Chem. and Ind.*, 1964, 1584.

[7] W. L. Marshall and J. S. Gill, *J. Inorg. Nuclear Chem.*, 1961, **22**, 115.

all the solutions. All the sodium phosphate mixtures were prepared freshly for each experiment from anhydrous $Na_2[HPO_4]$, dried at 110 °C, together with calculated quantities of standard Na[OH] or H_3PO_4 solutions. This $Na_2[HPO_4]$ was also used as a calibration standard in the analyses.

Sodium was determined in the range 2×10^{-5}—8×10^{-5} mol dm^{-3} by a method using a specific-ion electrode.[8] Diethylamine, rather than ammonia, vapour was used as the buffer, and the system was kept at 25 ± 0.2 °C. Phosphate was determined colorimetrically, over a similar concentration range, by the molybdate–vanadate method described in a British Standard.[9] A Unicam SP 1800 spectrophotometer was used. Some analyses for total phosphate were carried out on samples which had been boiled with dilute HNO_3 to hydrolyse pyrophosphates or other condensed phosphates. A ratio, P (as $Na_4[P_2O_7]$): total P of *ca.* 1 : 50 represented the limit of detection by this method for pyrophosphate in mixtures with orthophosphate.

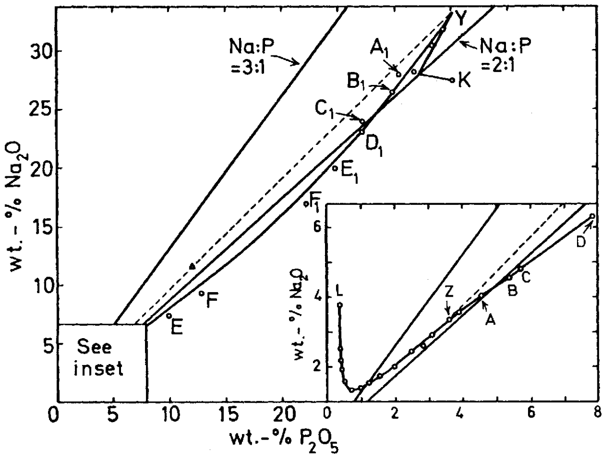

FIGURE 1 Solubility isotherm for the system Na_2O–P_2O_5–H_2O at 300 °C. The inset shows the low-solubility region plotted on an expanded scale. A and A_1 and B and B_1, *etc.*, are the compositions of conjugate solutions, Y and Z are invariant points, and K and L are the limits of the experimental measurements. (— — —), Tie line with point (△) representing overall composition

RESULTS

Preliminary experiments at both temperatures showed that equilibrium was apparently reached in a few hours, as there was no significant change of concentration with time when solutions were sampled at intervals between 4 and 24 h after reaching the working temperature. Normally, the solutions were left overnight to equilibrate (*ca.* 18 h), and the autoclaves were rocked. However, it was later found that it was unnecessary to rock the autoclaves in order to establish equilibrium overnight, so in the experiments designed to isolate solids the solutions remained static throughout.

Most of the experimental points on the solubility isotherms represent averages of two or three results, accurate to ±5—6% of the particular concentration value. Errors are higher, 8—10%, with the less accurate sampling technique employed for the more concentrated solutions.

Solubility at 300 °C.—The solubility isotherm is shown in Figure 1. The most significant feature of this diagram is the existence of a region (YZA—A_1) where two immiscible liquids are in equilibrium. This behaviour is unusual in aqueous electrolyte systems, but we consider the evidence for it to be strong, being based on the following observations.

Attempts to obtain solutions Z—F, using the technique whereby solutions Z—L were sampled, involving extraction of the saturated solution from the lowest point of the autoclave through a filter, always failed because a glassy solid blocked the sampling lines. However, a minor modification of the sampling technique, where the saturated solution was taken from a point well above the bottom of the autoclave, solved this problem. This behaviour is difficult to explain on the assumption that a solid is in equilibrium with solutions Z—F. It is readily explained if the equilibrium involves two immiscible liquids, one containing a high concentration of phosphate. Solids could be successfully isolated only from compositions giving solutions in the low-solubility region Z—L. No solids could be obtained from compositions in the region YZA—A_1; the small autoclaves were empty at the end of the experiments, during which both liquids must have been expelled to the atmosphere.

It was observed that two liquid layers appeared when initially homogeneous solutions with compositions in the region YZA—A_1 were heated in sealed Pyrex capillary tubes to *ca.* 300 °C. The glass was attacked fairly rapidly under these conditions, and became opaque after *ca.* 30 min. Collection of the denser liquid for analysis was achieved by allowing it to drain under gravity, after equilibrium had been reached, into a detachable plug fitted to a 73-cm^3 autoclave. The vessel was then removed from the furnace and rapidly cooled to room temperature.

Tie-lines could be constructed, using the compositions of the saturated solutions and of the corresponding initial mixtures. The latter were prepared between 25 and 60 °C, and their concentrations would change as the mixtures were heated in the closed autoclaves to the working temperature, largely due to the loss of water to the vapour space. A method of correcting for this has been described,[10] but in the present experiments correction factors did not exceed *ca.* 1.05 and the effect produced only negligible changes in the gradients of tie-lines. Tie-lines from saturated solutions in the low-solubility region indicated that the solid in equilibrium with these solutions was not $Na_3[PO_4]$, $Na_2[HPO_4]$, or a hydrate of either salt. As a working hypothesis, a formula $Na_rH_{3-r}PO_4$ was assumed for the solid; all the results from this region gave an average value for r of 2.75 ± 0.04. When solid samples were isolated and analysed the results confirmed this type of formula (Table 1). The most alkaline mixtures were not examined in these experiments as there was a risk of stress corrosion of the stainless-steel autoclaves under these conditions. Pyrophosphate or other condensed phosphates could not be detected in the solid. Other properties of this solid will be discussed later.

Tie-lines from saturated solutions in the region YK indicated that the solid phase here had a Na : P ratio of *ca.* 2 : 1. When a rapidly chilled equilibrium mixture was chemically analysed appreciable amounts of condensed phosphate, equivalent to a $Na_4[P_2O_7]$ content of 55%, were found. *X*-Ray data from a similar mixture (Table 2)

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[8] H. M. Webber and A. L. Wilson, *Analyst*, 1969, **94**, 209.

[9] B.S. 2690, 1966, part 3.

[10] A. S. McKie, ' Autoclave Correction Factors,' Internat. Conf. High Temperature, High Pressure Electrochemistry in Aqueous Solutions, University of Surrey, January 1973, National Association of Corrosion Engineers, Houston, paper D6, in the press.

could best be interpreted on the assumption that it contained $Na_4[P_2O_7]$, $Na_2[HPO_4]$, $Na_2[HPO_4]\cdot 2H_2O$, and $Na_2[HPO_4]\cdot 7H_2O$. Since pyrophosphate could not be found in the saturated solutions Y—K, we conclude that it is the solid phase at 300 °C, the other three compounds having crystallised during cooling.

TABLE 1

Composition of solids isolated from saturated solutions at 251 and 300 °C *

Saturated solution			Solid			
wt. %		$Na_2O : P_2O_5$	wt. %			$Na_2O : P_2O_5$ mol ratio
Na_2O	P_2O_5	mol ratio	Na_2O	P_2O_5	H_2O †	
1.70	0.43	9.05	53.6	43.4	3.0	2.82
1.40	0.60	5.34	53.2	43.3	3.5	2.81
1.62	1.32	2.80	51.4	43.2	5.4	2.73
2.00	1.97	2.33	52.2	43.3	4.5	2.76
2.29	2.43	2.15	52.6	43.8	3.6	2.75
3.36	3.59	2.14	52.4	43.6	4.0	2.76
3.36	3.59	2.14	50.2	43.1	6.7	2.66
6.51	2.15	6.94	53.1	44.2	2.7	2.75
4.55	3.15	3.31	51.6	44.2	4.2	2.68
10.5	9.99	2.41	50.4	43.8	5.8	2.64
Average composition of solid:			52.1	43.6	4.3	2.74

* First 7 results at 300 °C, remainder at 251 °C. † By difference.

TABLE 2

X-Ray powder diffraction data for rapidly cooled equilibrium mixtures from 300 °C and for various sodium phosphates

Mixture §		$Na_4[P_2O_7]$ *		$Na_2[HPO_4]$ *		$Na_2[HPO_4]\cdot 2H_2O$ *		$Na_2[HPO_4]\cdot 7H_2O$ *	
d(Å)	I/I_1 ‡	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1
8.38	5					8.42	60		
6.43	<5								
6.06	5							6.05	20
5.50	10							5.51	25
5.23	15					5.28	75	5.20	20
4.65	35	4.67	11	4.64	5	4.64	85	4.70	60
4.40	100	4.41	100			4.40	9		
4.23	20							4.25	80
								4.22	60
3.97	40			3.98	45	3.95	25		
3.83	45	3.84	7	3.84	55				
3.67	<5					3.66	20		
3.46	5			3.42	20			3.44	15
3.37	40	3.37	35			3.36	100	3.35	13
3.27	15					3.26	55	3.27	25
3.14	<5							3.15	9
3.02	10					3.01	20	3.025	40
2.942	5					2.945	25		
2.910	5					2.926	40	2.917	65
2.869	25			2.88	40	2.871	65	2.860	35
2.812	65			2.805	100			2.822	100
2.778	65					2.782	15	2.751	35
2.732 †	95	2.734	60	2.730	50	2.742	45		
2.684	80	2.698	70	2.720	25				
2.642	5	2.648	15	2.655	20				
2.582	5	2.592	5			2.594	25	2.579	30
2.529	5			2.537	7	2.493	30	2.527	15
2.437	15	2.440	9	2.453	17			2.473	30
2.324	35	2.336	25	2.320	7			2.333	13
2.196	20			2.197	9			2.193	11
2.071	20	2.073	15	2.068	7			2.035	40
1.985	15			1.988	7			1.986	15
1.920	50	1.921	20	1.921	17				

* Data from A.S.T.M. Index. † Broad line. ‡ Visual estimations of intensities. § 40% P_2O_5, Na : P = 2.0.

The solubility results enable two three-phase (excluding vapour) regions of composition to be defined on the Na_2O–P_2O_5–H_2O phase diagram at 300 °C. We have not marked these on Figure 1 in order to avoid the necessity of a reduction in scale and loss of clarity, but they would be the triangular areas SYZ and SYT, the points S and T denoting the compositions of the isolated solid and $Na_4[P_2O_7]$ respectively. In triangle SYZ the three phases would be solid S and the two liquids Y and Z, whereas the equilibrium mixture resulting from compositions within SYT would be solid S, $Na_4[P_2O_7]$, and liquid Y.

Solubility at 251 °C.—No region of immiscibility was found in the range of saturated solutions shown on the solubility isotherm in Figure 2. Extrapolation of tie-lines from solutions X—M indicated that a solid phase of Na : P ratio 2.83 ± 0.05 : 1 was in equilibrium. The three solid samples isolated and analysed (see Table 1) contained a slightly lower ratio, *ca.* 2.69 : 1. We consider that saturated solutions along XN are in equilibrium with $Na_2[HPO_4]$. This was found by *X*-ray analysis to be the major constituent of the rapidly cooled equilibrium mixture (40% P_2O_5, Na : P = 2.0 : 1). Trace amounts of $Na_4[P_2O_7]$ and $Na_2[HPO_4]\cdot 2H_2O$ were also present.

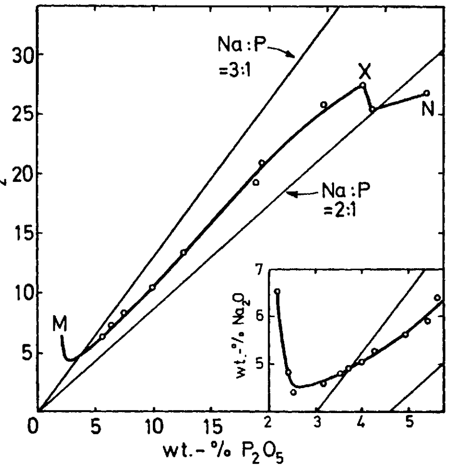

FIGURE 2 Solubility isotherm for the system Na_2O–P_2O_5–H_2O at 251 °C. The inset shows the low-solubility region plotted on an expanded scale. X is an invariant point, and M and N are the limits of the experimental measurements

Only one three-phase area on the phase diagram for this temperature was found for the range of compositions studied. Two solid phases, $Na_2[HPO_4]$ and the isolated solid, will be in equilibrium with liquid X for mixtures of composition within the triangle whose vertices correspond to the compositions of the three phases.

DISCUSSION

Properties of the Isolated Solids.—The solids isolated in the experiments summarised in Table 1 were always found as colourless hexagonal-shaped crystals, which were readily soluble in cold water and left no residue. One sample was analysed for Fe, but only 0.007% was found.

TABLE 3

X-Ray powder diffraction data for isolated solid (Cu-K_α radiation)

d(Å)		d(Å)	
6.80, 6.00, 5.82, 4.42	VW	2.56	M
4.25	VS	2.38, 2.33, 2.25, 2.19	VW
3.78, 3.69, 3.49, 3.29, 3.10, 2.88	VW	2.07	W
2.79	M	2.03, 2.00	VW
2.65	VS	1.89, 1.84	W
2.61	W	1.82, 1.79, 1.75, 1.61, 1.54, 1.52	VW

VS, Very strong; M, Medium; W, Weak; VW, Very weak.

The Na : P ratio in these solids apparently varied between 2.64 and 2.82 : 1, but they all gave identical *X*-ray powder photographs. Table 3 shows the *X*-ray data, which cannot be correlated with A.S.T.M. powder-diffraction data for sodium phosphates. No attempt was made to calculate the symmetry and dimensions of the unit cell in the crystals from these *X*-ray results. Lattice parameters for a narrow range of solid solutions may vary so little that the resulting *X*-ray patterns are not easily distinguishable. A brief study of the dehydration of samples of the solid was undertaken to ascertain whether any differences in behaviour occurred.

Solid samples were heated to 500 °C for several hours, which was found to be sufficient for complete reaction. Some conversion of orthophosphate into condensed phosphate took place, as the $Na : PO_4$ ratios in the samples increased, falling in the range 3.20—3.29. Differences amongst dehydration products from different initial samples seem to be small, and may be due to experimental error in the limited number of samples studied. It therefore seems likely that the solid in equilibrium with saturated solutions in the low-solubility regions at both temperatures is of constant, rather than variable, composition.

It can be seen from Table 1 that the average Na : P ratio from all the 10 solids analysed is 2.74 : 1. The compound $Na_{2.74}H_{0.26}PO_4$ contains only 1.4% water, appreciably less than the average of the samples in Table 1. It is unlikely that the water found in the chemical analysis arises from contamination by condensed steam of the compound $Na_{2.74}H_{0.26}PO_4$, because solid samples heated in a thermobalance do not begin to lose weight until a temperature of 330 °C is reached. If all the water found is not due to contamination, an empirical formula $2.74Na_2O\cdot P_2O_5\cdot 0.78H_2O$ fits the results well. The slightly simpler formula $11Na_2O\cdot 4P_2O_5\cdot 3H_2O$ is also consistent with these results, within experimental error. This formula can be rewritten to express the solid as a hydrated double salt of $Na_3[PO_4]$ and $Na_2[HPO_4]$, *i.e.* $3Na_3[PO_4]\cdot Na_2[HPO_4]\cdot H_2O$, or as a complex salt containing Na[OH], similar to that found at 0—60 °C, *e.g.* $Na_{2.5}H_{0.5}PO_4\cdot 0.25Na[OH]$. Such representations are not very satisfactory in this case because they imply that the solid would behave as a mixture of phosphate salts on dehydration. For example, the compound $3Na_3[PO_4]\cdot Na_2[HPO_4]\cdot H_2O$ might be expected to dehydrate to a mixture of $Na_3[PO_4]$ and $Na_4[P_2O_7]$. However, the *X*-ray pattern of the reaction products could not be interpreted from data on sodium phosphates in the A.S.T.M. Index, and the $Na : PO_4$ ratio of such a mixture would be 3.67 : 1 which is significantly larger than that observed.

Solubility of $Na_3[PO_4]$.—Our results fall about midway between those reported earlier,[3,4] which differ from each other by *ca.* 20%. Schroeder *et al.*[3] isolated, but did not analyse, the solid from these solutions, considering it to be anhydrous $Na_3[PO_4]$. Ravich and Shcherbakova[4] concluded, from an indirect method, that the solid had a Na : P ratio of *ca.* 2.85 : 1. It now seems clear that $Na_3[PO_4]$ does not crystallise from solutions of Na : P ratio 3 : 1 at these elevated temperatures. A sharp change of gradient was found in the solubility curve for trisodium phosphate at 215 °C;[3] this probably marks the transition temperature below which the solid of Na : P ratio *ca.* 2.75 : 1 cannot be crystallised. If this assumption is correct, then solids of Na : P ratio 3 : 1 are stable in saturated solutions of the same ratio only in the range 55—215 °C.[1,3] A more acidic compound crystallises at high temperatures, whilst a more alkaline complex (Na : P = 3.25 : 1) is the stable phase below 55 °C.[1]

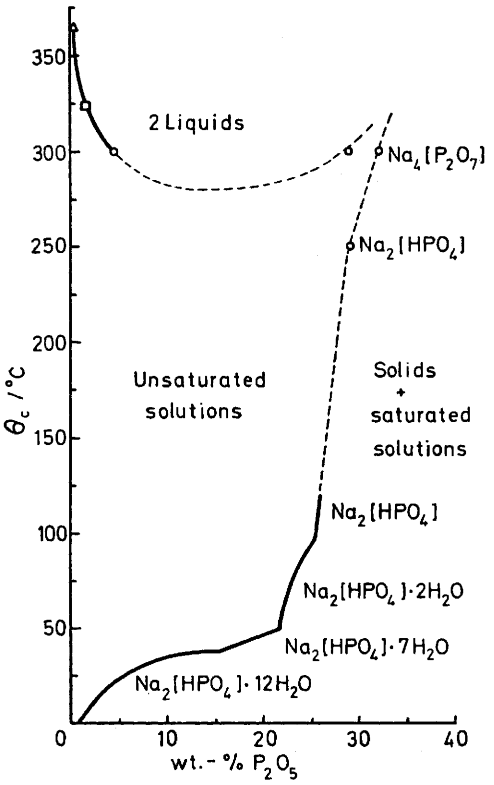

FIGURE 3 Solubility of $Na_2[HPO_4]$ (DSP) as a function of temperature. (——), Experimental solubility data; (— — —), estimated behaviour; (○), this work; (△), ref. 4; (□), ref. 5

Solubility of $Na_2[HPO_4]$.—Our solubility values at 300 °C are generally in good agreement with those of Panson *et al.*[5] However, their conclusion that a solid of variable composition is in equilibrium with saturated solutions with Na : P ratios less than *ca.* 2.13 : 1 is not consistent with our findings. We believe that the solubility of $Na_2[HPO_4]$ between 0 and 365 °C can best be represented as in Figure 3, which has been constructed using data from a number of sources[1,4,5,11] as well as the results reported here. The solubility of the salt at 275 °C could not be measured accurately, but is no lower than the value indicated by the right-hand broken curve in Figure 3.[5] It can be seen that this is too high to lie on the liquid–liquid curve, which therefore cannot extend down to 275 °C. Discontinuities in the solubility isotherms where they cross the line of Na : P ratios of 2 : 1 have been noted[1] at temperatures below 100 °C, and it can be seen from Figures 1 and 2 that they occur at 250 and 300 °C. They are considered to be sharp discontinuities rather than rounded minima.[1]

Liquid–liquid immiscibility has been observed in several aqueous electrolyte systems including $PbBr_2$–H_2O above 302 °C,[12] Na_2O–SiO_2–H_2O at 250—350 °C,[13] UO_3–SO_3–H_2O above 290 °C,[14,15] and the $K_2[SO_4]$–$KLi[SO_4]$–H_2O system above 300 °C.[16] In all these cases the concentration of the dilute liquid decreases, and that of the concentrated liquid increases, as the temperature is increased. The immiscible liquids in the $Na_2[HPO_4]$–H_2O system are assumed to behave similarly. Analogous phenomena occur in electrolyte solutions in solvents of low dielectric constant at *ca.* 25 °C, and an explanation has been given in terms of electrical forces among ion pairs.[17] This mechanism may also apply to the aqueous electrolyte systems at high temperatures, since the dielectric constant of water under these conditions is only *ca.* 25% of the value at 25 °C and atmospheric pressure.[18]

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[11] A. Seidell and W. F. Linke, ' Solubilities of Inorganic and Metal Organic Compounds,' 4th edn., American Chemical Society, Washington, D.C., vol. 2.

[12] A. Benrath, F. Gjedebo, B. Schiffers, and H. Wunderlich, *Z. anorg. Chem.*, 1937, **231**, 285.

[13] O. F. Tuttle and I. Friedman, *J. Amer. Chem. Soc.*, 1948, **70**, 923.

[14] C. H. Secoy, *J. Amer. Chem. Soc.*, 1950, **72**, 3343.

[15] E. V. Jones and W. L. Marshall, *J. Inorg. Nuclear Chem.*, 1961, **23**, 287.

[16] M. I. Ravich and V. M. Valyashko, *Russ. J. Inorg. Chem.*, 1969, **14**, 864.

[17] H. L. Friedman, *J. Phys. Chem.*, 1962, **66**, 1595.

[18] K. Tödheide, in ' Water, a Comprehensive Treatise,' ed. F. Franks, Plenum Press, New York, 1972, vol. 1.