

COMPONENTS: (1) Sodium dihydrogenphosphate; NaH_2PO_4 ; [7553-80-7] (2) Water; H_2O ; [7732-18-5]	EVALUATOR: J. Eysseltoová Charles University Prague, Czechoslovakia May 1985
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CRITICAL EVALUATION:

The values reported for the solubilities in multicomponent systems containing sodium dihydrogenphosphate will be presented, and, where possible, evaluated in this chapter.

Ternary systems with two saturating components

Seven such systems have been studied, but in several of these reports, there are insufficient data to permit a critical evaluation to be made. There was no evidence for the formation of solid solutions and/or solid ternary compounds in any of these systems. Critical evaluations will be made for the following four systems.

1. The NaH_2PO_4 - NaBO_3 - H_2O system. This system has been studied at 298 and 308 K (1). The appearance of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ [61028-24-8] as one of the solid phases in this system indicates that the system cannot be treated as a ternary one, but should be considered as a part of the Na_2O - B_2O_3 - P_2O_5 - H_2O system.

2. The NaH_2PO_4 - NaNO_3 - H_2O system. Solubility data for this system have been obtained at 273, 283, 293 and 303 K (2), and at 323 K (3). The solubility data for the isotherms at 273, 283 and 293 K can be described by equation [1], derived by Kirgintsev (4). In this equation, m_1 is the molality of the salt, m_0 is the molality of the same salt in a

$$\log(m_1/m_0) = (-1/\alpha)\log y_1 \quad [1]$$

saturated aqueous solution under the same conditions, y_1 is the solute mole fraction of the component, and α is an adjustable parameter. In an ideal solution $\alpha = da_w/dm$ where a_w is the activity of the water and m is the molality of the component. The values of $(-1/\alpha)$ for this system are given in Table I.

Table I. Parameters of equation [1] for the NaH_2PO_4 - NaNO_3 - H_2O system.

T/K	NaH_2PO_4		NaNO_3	
	$-1/\alpha$	σ^α	$-1/\alpha$	σ^α
273	0.68	0.02	1.03	0.06
283	0.70	0.02	0.98	0.03
293	0.68	0.03	0.88	0.06

σ^α the standard deviation of the $(-1/\alpha)$ value

The data at 303 K (2) and at 323 K (3) do not give a constant value for α . This is possibly due to some interaction between the two salts at these higher temperatures, whereas in the derivation of equation [1] it was assumed that there is no such interaction. Figure 1 is a summary of the solubility data obtained experimentally and by the use of equation [1].

3. The NaH_2PO_4 - NaCl - H_2O system. Solubility data for this system were reported for 273, 298 and 348 K (5), at 298 and 323 K (6), and at 313 K (7). Of all these data only the 298 K isotherms (5, 6) can be compared directly, Figure 2. The solubility of NaH_2PO_4 can be expressed by equation [2]. Neither the solubility of NaH_2PO_4 at other temperatures nor the solubility of NaCl can be expressed by equation [1]. Attempts to use

$$\log m_1 = \log 7.7 - (1.1 \pm 0.1) \log y_1 \quad [2]$$

equation [1] gave values for α that either varied or had standard deviations of about 50%.

4. The NaH_2PO_4 - KH_2PO_4 - H_2O system. Babenko and Vorob'eva (8) present solubility data from which it is possible to construct a polytherm and make comparison with data obtained by others for solutions simultaneously saturated with two solids (5, 7). This is done on Figure 3. The agreement is fairly good. However, equation [1] could not be used for this system because it was impossible to obtain a constant value for α . This is likely due to the fact that equation [1] was derived on the basis of simplifying assumptions and this system is too complex for such assumptions to be valid. A more precise model is needed but this may require additional parameters. At present there are too few data available to calculate values for additional parameters.

Three other ternary systems have been studied but only a limited amount of experimental data is available. Therefore, no evaluation of these data can be made.

(continued next page)

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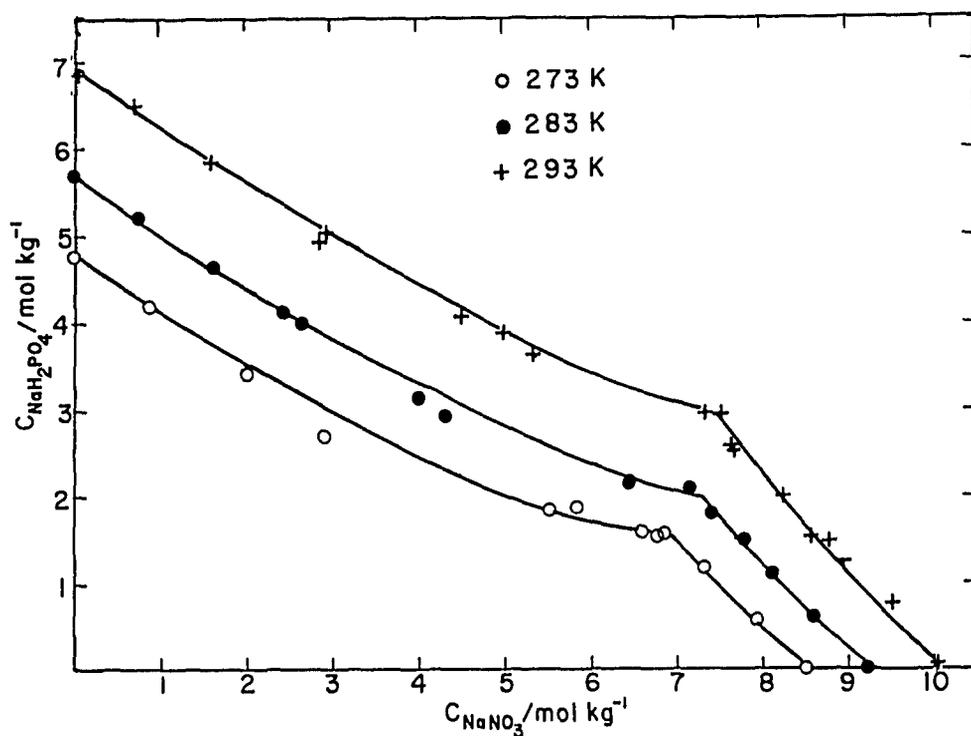


Figure 1. Solubility in the NaH_2PO_4 - NaNO_3 - H_2O system. The solid lines represent equation [1].

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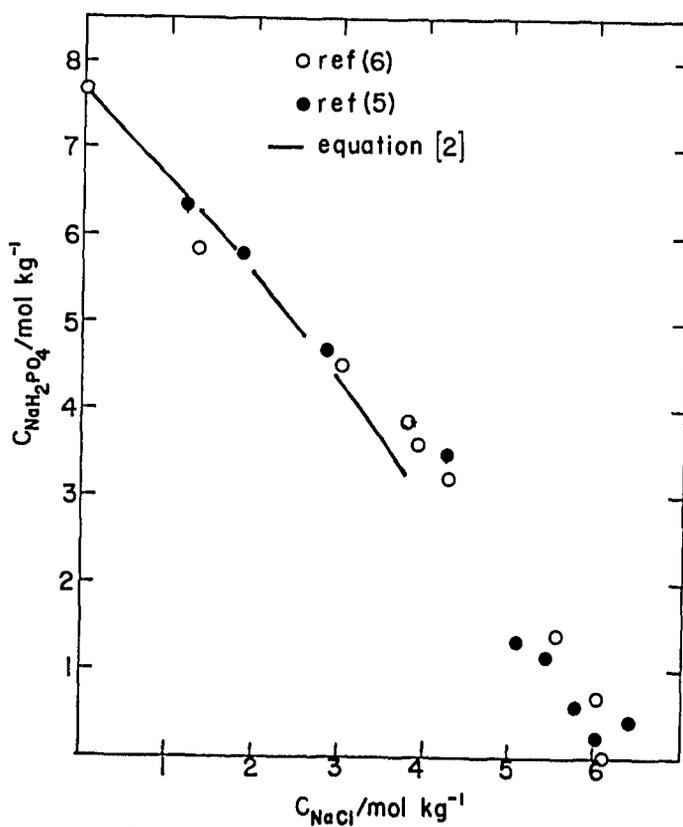
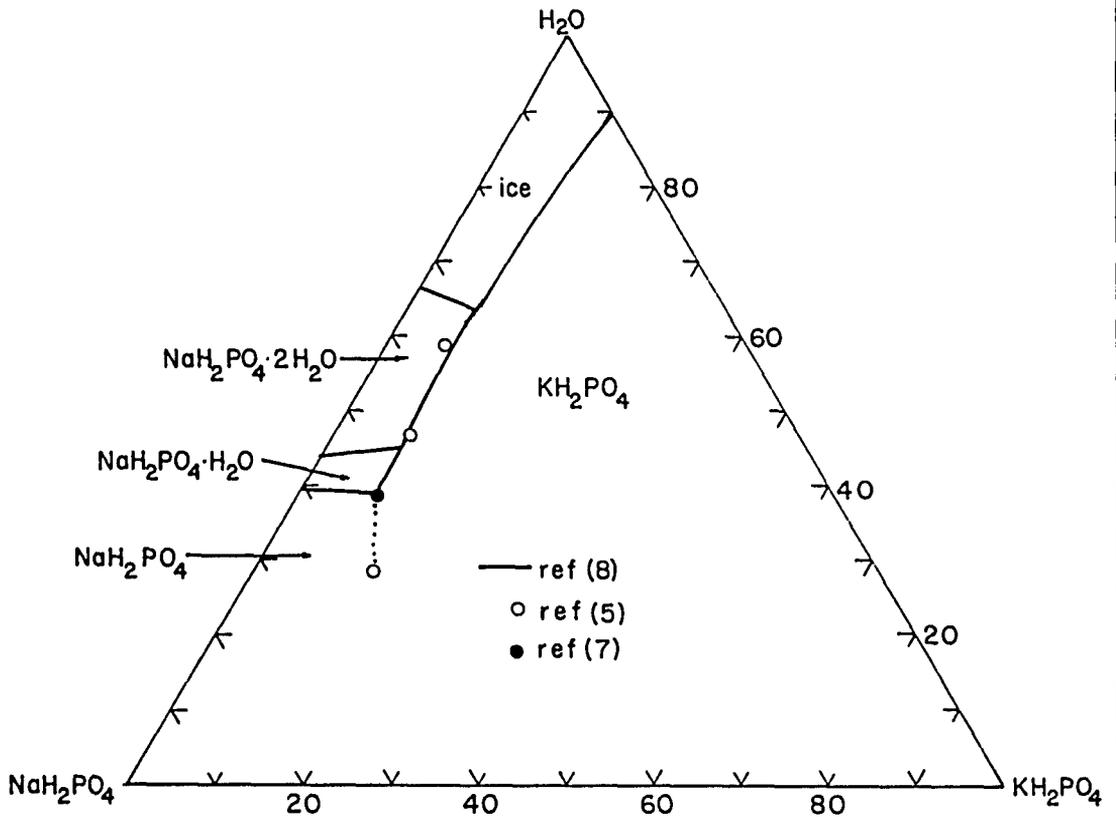


Figure 2. Solubility in the NaH_2PO_4 - NaCl - H_2O system at 298 K.

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Figure 3. Solubility in the NaH_2PO_4 - KH_2PO_4 - H_2O system.

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<p>CRITICAL EVALUATION: (cont'd)</p> <p>These other systems are: NaH_2PO_4-Na_2SO_4-H_2O studied at 298 K (9); NaH_2PO_4-NaClO_4-H_2O studied at 298 K (10); and NaH_2PO_4-$\text{NH}_4\text{H}_2\text{PO}_4$-$\text{H}_2\text{O}$, studied at 263 to 303 K (11).</p> <p style="text-align: center;">Systems having an organic component</p> <p>Solubility data for the NaH_2PO_4-acetone-H_2O system and for two sections through the NaH_2PO_4-NaClO_4-acetone-H_2O system at 298 K have been reported (12). Layer formation was observed in all the studies. Not enough data are available to make a critical evaluation of the work. However, the value reported for the solubility of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ in water at 298 K is in error by about +20%.</p> <p style="text-align: center;">Quaternary systems</p> <p>Solubility data have been reported for four quaternary systems: (a) a section through the NaH_2PO_4-$\text{NH}_4\text{H}_2\text{PO}_4$-$(\text{NH}_4)_2\text{HPO}_4$-$\text{H}_2\text{O}$ system at 262 to 343 K (13); (b) three isotherms of the Na^+, $\text{K}^+ \text{H}_2\text{PO}_4^-$, NO_3^--H_2O system (14); (c) the Na^+, $\text{NH}_4^+ \text{H}_2\text{PO}_4^-$, Cl^--H_2O system at 298 K (15); and (d) the Na^+, $\text{K}^+ \text{H}_2\text{PO}_4^-$, Cl^--H_2O system at 298 K (15), at 313 K (7), and at 273, 298, 323 and 373 K (16).</p> <p>The 298 K solubility isotherm for the Na^+, $\text{K}^+ \text{H}_2\text{PO}_4^-$, Cl^--H_2O system is given on Figure 4. The values given for the boundary ternary systems are those reported for the eutonic solutions in the NaH_2PO_4-NaCl-H_2O system (5, 6), the NaH_2PO_4-KH_2PO_4-H_2O system (5), the KH_2PO_4-KCl-H_2O system (17-19), and the KCl-NaCl-H_2O system (20). There appears to be a systematic error in the data of Brunisholz and Bodmer (16). The phosphate content is too large. Therefore, the data of Solov'ev, et al. (15) are preferred.</p> <p style="text-align: center;">References</p> <ol style="list-style-type: none"> Beremzhanov, B.A.; Savich, R.F.; Kunanbaev, G.S. <i>Khim. Khim. Tekhnol. (Alma Ata)</i> 1977, <i>22</i>, 15. Shpunt, S.J. <i>Zh. Prikl. Khim.</i> 1940, <i>13</i>, 19. Kol'ba, V.I.; Zhikharev, M.I.; Sukhanov, L.P. <i>Zh. Neorg. Khim.</i> 1981, <i>26</i>, 828. Kirgintsev, A.N. <i>Izv. Akad. Nauk SSSR, Ser. Khim. Nauk</i> 1965, <i>8</i>, 1591. Brunisholz, G.; Bodmer, M. <i>Helv. Chim. Acta</i> 1963, <i>46</i>, 288, 2566. Girich, T.E.; Gulyamov, Yu. M.; Ganz, S.N.; Miroshina, O.S. <i>Vopr. Khim. Khim. Tekhnol.</i> 1979, <i>57</i>, 58. Khallieva, Sh. D. <i>Izv. Akad. Nauk Terkm. SSSR, Ser. Fiz.-Tekh., Khim. Geol. Nauk</i> 1977, <i>3</i>, 125. Babenko, A.M.; Vorob'eva, T.A. <i>Zh. Prikl. Khim (Leningrad)</i> 1975, <i>48</i>, 2437. Apfel, O. Dissertation, Technical University, Darmstadt 1911. Lilich, L.S.; Alekseeva, E.A. <i>Zh. Neorg. Khim.</i> 1969, <i>14</i>, 1655. Shpunt, S.J. <i>Zh. Prikl. Khim.</i> 1940, <i>13</i>, 9. Ferroni, G.; Galea, J. Antonetti, G. <i>Bull. Soc. Chim. Fr</i> 1974, <i>12</i> (Pt. 1), 273. Babenko, A.M.; Vorob'eva, T.A. <i>Zh. Prikl. Khim.</i> 1976, <i>49</i>, 1502. Girich, T.E.; Gulyamov, Yu. M. <i>Vopr. Khim. Khim. Tekhnol.</i> 1979, <i>57</i>, 54. Solov'ev, A.P.; Balashova, E.F.; Verendyakina, N.A.; Zyzina, L.F. <i>Resp. Sb. Nauch. Tr.-Yaroslav. Gos. Ped. In-t.</i> 1978, <i>169</i>, 79. Brunisholz, G.; Bodmer, M. <i>Helv. Chim. Acta</i> 1963, <i>46</i>, 289, 2575. Krasil'shtchikov, A.I. <i>Izv. In-ta Fiz.-Khim. Anal.</i> 1933, <i>6</i>, 159. Filipescu, L. <i>Rev. Chim. (Bucharest)</i> 1971, <i>22</i>, 533. Mraz, R.; Srb, V.; Tichy, D.; Vosolsobe, J. <i>Chem. Prum.</i> 1976, <i>26</i>, 511. Seidell, A. <i>Solubilities of Inorganic and Metal Inorganic Compounds</i>, D. Van Nostrand Co., New York 1953. 	

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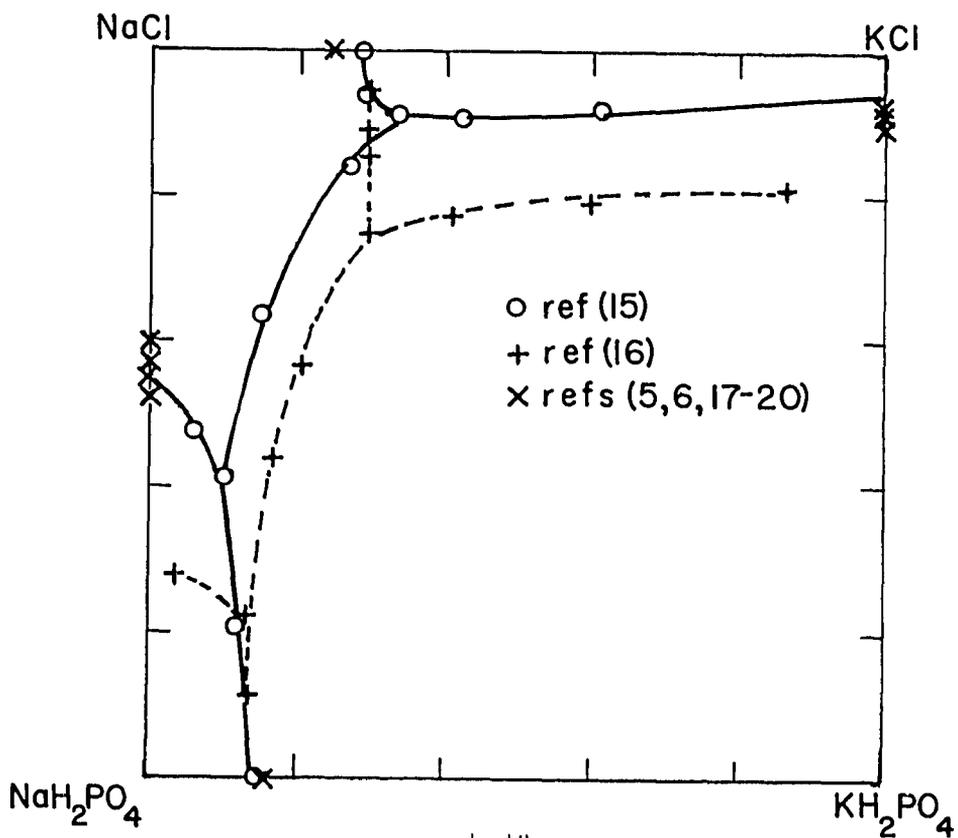


Figure 4. Solubility in the $\text{Na}^+, \text{K}^+ || \text{H}_2\text{PO}_4^-, \text{Cl}^- - \text{H}_2\text{O}$ system at 298 K.