

Physico-chemical properties of phosphate solutions used in KDP single crystal growth

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Basing on known experimental data, mathematical dependences have been derived for determination of the solution compositions in the $K_2O-P_2O_5-H_2O$ system. Equations have been proposed to calculate the solubility and the density of the saturated KH_2PO_4 solutions within wide ranges of the solution pH and temperature. The ion equilibrium calculations for KH_2PO_4 phosphate solutions evidence the formation possibility of protonated phosphate dimer forms that favor the KH_2PO_4 solubility increase. The results obtained supply the known literature data on the acidity effect on the composition and physicochemical properties of the $K_2O-P_2O_5-H_2O$ system solutions and could be applied to optimize the growing conditions of KDP single crystals from aqueous solutions.

На основе известных экспериментальных данных получены математические зависимости для определения составов растворов в системе $K_2O-P_2O_5-H_2O$. Предложены уравнения расчета растворимости и плотности насыщенных растворов KH_2PO_4 в широком диапазоне изменения pH и температуры раствора. Расчеты ионного равновесия в фосфорнокислых растворах KH_2PO_4 показали возможность образования протонированных фосфат-димерных форм, которые способствуют повышению растворимости KH_2PO_4 . Полученные результаты дополняют известные из литературы сведения о влиянии кислотности на состав и физико-химические свойства растворов в системе $K_2O-P_2O_5-H_2O$ и могут найти применение для оптимизации условий выращивания монокристаллов KDP из водных растворов.

The electrooptical and nonlinear KDP single crystals grown from aqueous KH_2PO_4 solutions are used widely in modern engineering to control the high-power laser radiation. The solution acidity is among the most important parameters defining the KDP crystal growth and properties. The acidity variations influence the ionic composition, solubility of the components, the ortho-phosphate solution density, stability and other characteristics. The growth kinetics, morphology and physical properties of KDP crystals depend heavily on the hydrogen ion concentration in the working solution [1].

The acid-base equilibria in the ternary $K_2O-P_2O_5-H_2O$ system were studied by several authors [2–5]. It follows from the

phase diagram of the system (Fig. 1) that KH_2PO_4 is crystallized within a wide range of P_2O_5 concentration (10 through 47 % mass). The 0, 25, and 50°C isotherms show a pronounced knee at the $K_2O:P_2O_5 = 1:1$ composition axis with a minimum solubility in the singular point. The KH_2PO_4 solubility increases when the composition is deviated towards the acidic or basic region of the phase equilibrium. In [6, 7], presented are empirical temperature dependences of the KH_2PO_4 solubility. The saturated solution concentration as the temperature function is calculated as

$$c = (\alpha \exp[\beta t]) \cdot 100, \quad (1)$$

where c is the KH_2PO_4 concentration in kg/kg of solution; t , temperature in °C; α

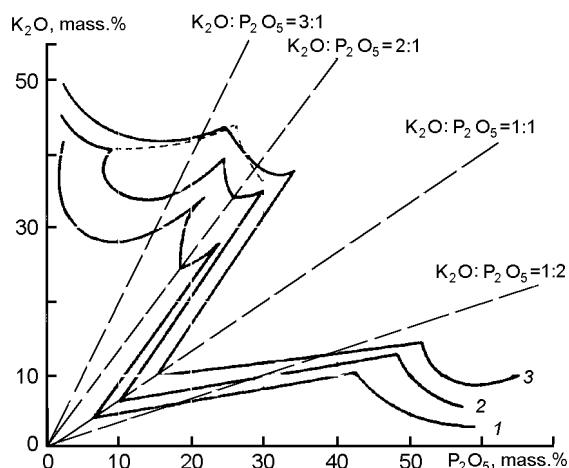


Fig. 1. Solubility isotherms in the $K_2O-P_2O_5-H_2O$ system [2-4]; 1 - 0°C, 2 - 25°C, 3 - 50°C.

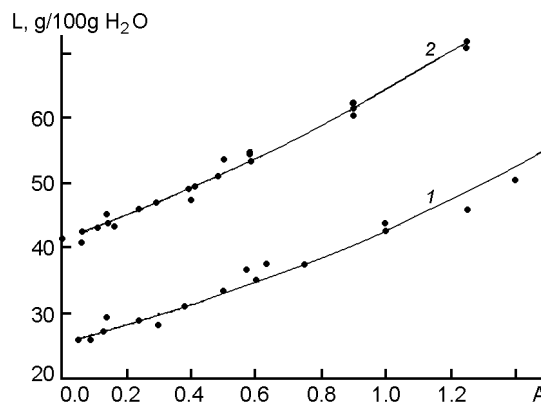


Fig. 2. KH_2PO_4 solubility as a function of the solution composition (pH < 4) at 25 (1) and 50°C (2).

and β , coefficients in the saturation line equation given in [6]. Eq.(1) is suitable only for KH_2PO_4 solutions in pure water. In [7], data are presented characterizing the KH_2PO_4 solubility in aqueous solutions containing H_3PO_4 or KOH admixtures at temperatures of 20 to 60°C. For each polytherm studied, the integrating polynomial is calculated:

$$c = a_{0i} + a_1t + a_2t^2, \quad (2)$$

where the KH_2PO_4 saturating concentration in g per 100 g H_2O ; t , temperature in °C; a_i , the polynomial coefficients corresponding to the solution composition [7]. The calculations show, however, that for some solution compositions, the data calculated using Eq.(2) differ substantially from experimental ones.

The solubility variation depending on the solution composition and temperature results in variations in its density. The density of multicomponent $KH_2PO_4-H_3PO_4-H_2O$ and $KH_2PO_4-K_3PO_4-H_2O$ solutions as a function of temperature can be calculated using the following equation proposed in [6]:

$$\lg \rho = \lg \rho_0 + \sum_{i=1}^n A_i c_i, \quad (3)$$

where ρ and ρ_0 is the density of the multicomponent solution and water, respectively, in kg/m^3 ; c_i , the component concentration, kg/kg of solution; A_i , the temperature dependence of the component density calculable using the polynomial

$$A_i = a_{0i} + a_1t + a_2t^2. \quad (4)$$

The a_i values for KH_2PO_4 and K_2HPO_4 are given in [6]. There are no such data for H_3PO_4 , therefore, the density dependence for H_3PO_4 has been determined indirectly from the correlation dependence between H_2SO_4 and H_3PO_4 density [6].

To optimize the KDP crystal growing technology, it is reasonable to establish a correlation between the working solution acidity and other properties thereof, such as concentration, density, and ionic composition. To that end, this work summarizes experimental data [3-12] on the properties of the $K_2O-P_2O_5-H_2O$ system within wide ranges of pH (2.0 to 6.0) and temperature (20 to 80°C) and proposes mathematical expressions for some physicochemical characteristics of the solutions.

It is just the solubility isotherms in the $K_2O-P_2O_5-H_2O$ system at 25 and 50°C that have been studied most comprehensively. These experimental data have been processed using the least square method and a logarithmic dependence has been found to exist between the solution composition and the solubility at 25 and 50°C that is described by the following expressions, respectively:

$$\begin{aligned} &\text{for solutions with pH} < 4 \\ \ln L &= 0.52075A + 3.22963, \end{aligned} \quad (5)$$

$$\ln L = 0.44102A + 3.71768, \quad (6)$$

$$\begin{aligned} &\text{for solutions with pH} > 4 \\ \ln L &\equiv 2.12090B + 3.14704, \end{aligned} \quad (7)$$

$$\ln L = 2.13811B + 3.67186, \quad (8)$$

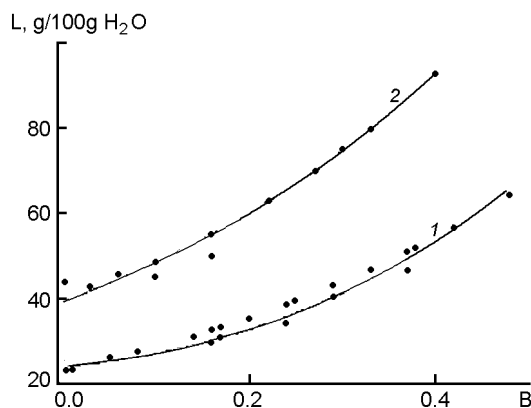


Fig. 3. KH₂PO₄ solubility as a function of the solution composition (pH > 4) at 25 (1) and 50°C (2).

Table 1. Coefficient values in (9)

Solution composition, g per 100 g water [7]	<i>a</i>	<i>b</i>
No additives	2.74830	1.87622·10 ⁻²
1.72 H ₃ PO ₄	2.78304	1.83622·10 ⁻²
5.0 H ₃ PO ₄	2.90321	1.73063·10 ⁻²
10.0 H ₃ PO ₄	3.07872	1.55983·10 ⁻²
15.0 H ₃ PO ₄	3.21340	1.50116·10 ⁻²
2.0 KOH	2.98356	1.62876·10 ⁻²
5.0 KOH	3.38789	1.25719·10 ⁻²
10.0 KOH	3.80893	9.49048·10 ⁻³
15.0 KOH	4.11919	7.62361·10 ⁻³

where *L* is the KH₂PO₄ solubility, g per 100 g H₂O; $A = m(\text{H}_3\text{PO}_4) / m(\text{KH}_2\text{PO}_4)$; $B = m(\text{K}_2\text{HPO}_4) / m(\text{KH}_2\text{PO}_4)$; *m* is the mole number per kg H₂O. The *L* values calculated according to (5)–(8) evidence that the solubility is lowest at the stoichiometric composition of the solution, K₂O: P₂O₅ = 1:1. The KH₂PO₄ solubility increases when the composition is deviated towards the acidic or basic region (Figs. 2 and 3). According to [9, 10], this phenomenon is due to formation of protonated phosphate associates in the solution. Fig. 4(a, b) illustrates the calculated data on the ionic composition of saturated KH₂PO₄ solutions as a function of the medium pH. In the calculations, the known formation constants of protonated phosphate associates [13, 14] have been

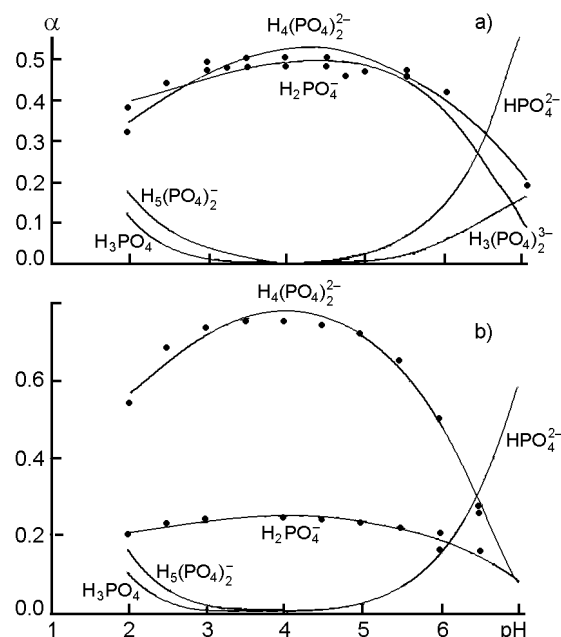


Fig. 4. Distribution of phosphate ion forms as a function of KH₂PO₄ solution pH at 25°C (a) and 70°C (b); α is the mole fraction.

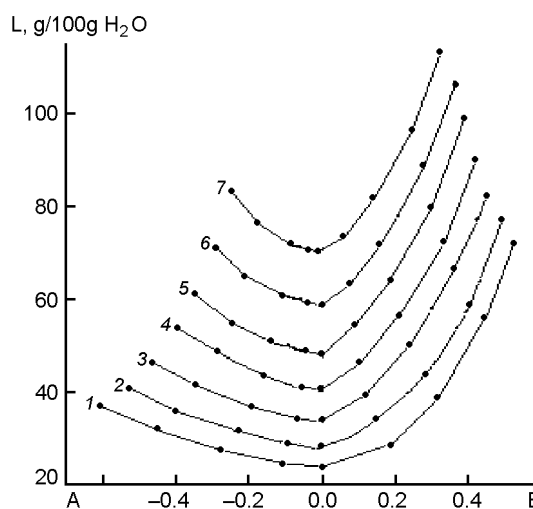


Fig. 5. KH₂PO₄ solubility isotherms in the K₂O–P₂O₅–H₂O system. $A = m(\text{H}_3\text{PO}_4) / m(\text{KH}_2\text{PO}_4)$; $B = m(\text{K}_2\text{HPO}_4) / m(\text{KH}_2\text{PO}_4)$. Temperature, °C: 20 (1); 30 (2); 40 (3); 50 (4); 60 (5); 70 (6); 80 (7).

used. The consideration of the results obtained has shown that it is just the H₂PO₄⁻ and the dimers thereof H₄(PO₄)₂²⁻ that predominate in aqueous KH₂PO₄ solution at pH = 4.0±0.2. As the solution temperature rises up to 70°C, the dimer fraction increases approximately thrice (Fig. 4b).

In acidic solutions, there are associates H₅(PO₄)₂⁻ along with monomeric H₃PO₄

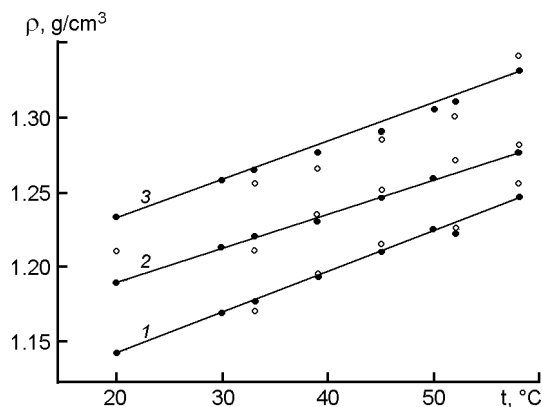


Fig. 6. KH_2PO_4 solution density as a function of temperature and pH. pH values: 4.0 (1), 5.0 (2), 5.5 (3). Light circles, experimental data [16]; dark circles, calculated values.

ions. In the solutions containing KOH admixture ($\text{pH} > 4$), the formation of $\text{H}_3(\text{PO}_4)_2^{3-}$ associate is typical. The anionic phosphate associates have been found to form stable neutral ion pairs with alkali metal cations [15]. The associate formation process is connected with water release from the hydrate shells of H_2PO_4^- ions [7], thus resulting in an increased solubility of KH_2PO_4 macroscale component. In the solutions with KOH additive, a disubstituted potassium phosphate admixture appears, that acts as a salting-in agent and favors further the KH_2PO_4 solubility.

Basing on the experimental data presented in [7], we have derived an empirical expression for the dependence of KH_2PO_4 solubility on the solution composition and temperature:

$$\ln L = a + bt, \quad (9)$$

where L is the KH_2PO_4 solubility, g per 100 g H_2O ; t , the temperature, $^\circ\text{C}$; a and b , coefficients corresponding to the solution composition (see Table 1). The KH_2PO_4 solubility isotherms calculated using (9) are presented in Fig. 5.

The density may provide an informative index of the phosphate solution state. The density is a function of the salt concentration, the solution temperature and acidity. Using the experimental data on the density of saturated KH_2PO_4 solutions [16], we have derived a logarithmic dependence of the density on the solution temperature and acidity:

$$\ln \rho = k + qt, \quad (10)$$

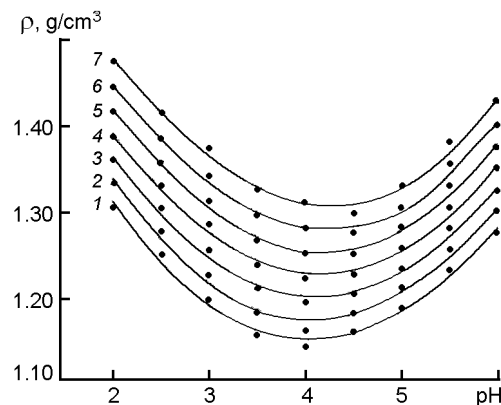


Fig. 7. KH_2PO_4 solution density isotherms in the $\text{K}_2\text{O}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ system. Temperature, $^\circ\text{C}$: 20 (1); 30 (2); 40 (3); 50 (4); 60 (5); 70 (6); 80 (7).

where ρ is the saturated KH_2PO_4 solution density, g/cm^3 ; t , the temperature, $^\circ\text{C}$; k and q , coefficients corresponding to different pH values (see Table 2). Fig. 6 presents the experimental and calculated values of the solution density at various pH values within temperature range of 20 to 60°C .

The density variations of saturated KH_2PO_4 solutions within the pH range of 2.0 to 6.0 are characterized by isotherms calculated using Eq.(10) and shown in Fig. 7. To determine the KH_2PO_4 solubility from the saturated solution density, we have proposed the equation

$$\ln L = m + n\rho, \quad (11)$$

that takes into account the dependence of those quantities on the solution acidity (see Table 2). The solubility and corresponding density values of saturated KH_2PO_4 solutions calculated basing on (10), (11) within

Table 2. Coefficient values in (10), (11)

pH(± 0.1)	k	$q \cdot 10^3$	m	n
2.0	0.26673	2.02772	-3.38549	5.28560
2.5	0.18312	2.05044	-4.01387	5.91247
3.0	0.13477	2.14913	-4.44516	6.44372
3.5	0.09445	2.28754	-4.36857	6.51552
4.0	0.08646	2.30211	-4.57585	6.74086
4.5	0.11212	1.86460	-5.07429	7.21992
5.0	0.13586	1.87115	-2.67755	5.31836
5.5	1017097	1.91186	-0.78119	3.87988
6.0	0.20639	1.87119	0.39618	3.03842

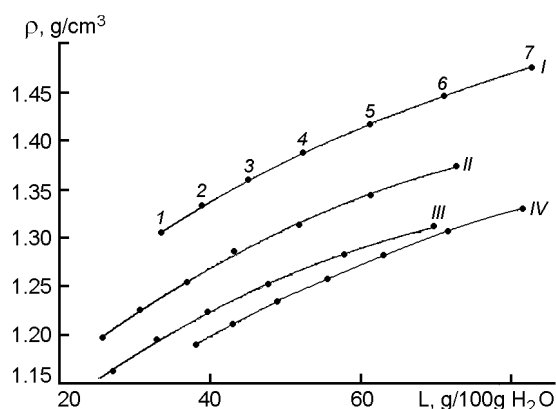


Fig. 8. Solubility and density polytherms for KH_2PO_4 solutions. Temperature, $^{\circ}\text{C}$: 20 (I); 30 (2); 40 (3); 50 (4); 60 (5); 70 (6); 80 (7). pH values: 2.0 (I), 3.0 (II), 4.0 (III), 5.0 (IV).

temperature range of 20 to 60°C are presented in Table 3 and Fig. 8.

Thus, basing on the known experimental data, mathematical expressions have been derived to determine the solution compositions in the $\text{K}_2\text{O}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ system. Equations are proposed to calculate the KH_2PO_4 solubility and the saturated solution density within wide ranges of the solution pH and temperature. The ion equilibrium calculations in KH_2PO_4 phosphate solutions have shown the formation possibility of pro-

tonated phosphate dimer forms favoring the enhanced KH_2PO_4 solubility. The results obtained supply the literature data on the acidity effect on the composition and physicochemical properties of the $\text{K}_2\text{O}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ system solutions and can be applied in optimization of the growing conditions of KDP single crystals from aqueous solutions.

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Table 3. Dependence of solubility L (g KH_2PO_4 per 100 g water) and density ρ (g/cm^3) for saturated KH_2PO_4 solutions on the solution temperature and pH

pH(± 0.1)	2.0		2.5		3.0		3.5		4.0	
$t^{\circ}\text{C}$	L	ρ	L	ρ	L	ρ	L	ρ	L	ρ
20	33.6	1.306	29.4	1.251	25.8	1.198	23.3	1.156	22.7	1.142
30	39.0	1.333	34.5	1.277	30.6	1.226	28.0	1.183	27.3	1.161
40	45.3	1.360	40.5	1.304	37.0	1.254	33.7	1.210	32.9	1.195
50	52.7	1.388	47.8	1.330	43.3	1.286	40.5	1.238	39.7	1.223
60	61.2	1.417	55.8	1.358	51.8	1.312	48.7	1.267	47.9	1.252
70	71.1	1.446	65.4	1.386	61.2	1.343	58.5	1.296	57.8	1.281
80	82.6	1.475	76.7	1.415	72.8	1.374	70.2	1.326	69.7	1.311
pH(± 0.1)	4.5		5.0		5.5		6.0			
$t^{\circ}\text{C}$	L	ρ	L	ρ	L	ρ	L	ρ		
20	27.5	1.161	38.4	1.189	54.5	1.233	72.1	1.276		
30	32.2	1.183	43.0	1.212	60.1	1.256	77.6	1.300		
40	37.9	1.205	40.1	1.235	66.2	1.281	83.5	1.325		
50	44.6	1.228	55.5	1.258	72.5	1.305	90.0	1.350		
60	52.5	1.251	63.1	1.282	80.3	1.331	97.2	1.375		
70	62.5	1.275	71.6	1.306	88.7	1.356	105.4	1.401		
80	73.8	1.298	81.5	1.330	97.9	1.382	114.4	1.428		

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Фізико-хімічні властивості фосфорнокислих розчинів, що використовуються для вирощування монокристалів KDP

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На основі відомих експериментальних даних отримано математичні залежності для визначення складу розчинів у системі $K_2O-P_2O_5-H_2O$. Запропоновано рівняння розрахунку розчинності та густини насичених розчинів KH_2PO_4 у широкому діапазоні змінення рН і температури розчину. Розрахунки іонної рівноваги у фосфорнокислих розчинах KH_2PO_4 показали можливість утворення протонованих фосфат-димерних форм, які сприяють підвищенню розчинності KH_2PO_4 . Одержані результати доповнюють відомі з літератури дані про вплив кислотності на склад та фізико-хімічні властивості розчинів у системі $K_2O-P_2O_5-H_2O$, а також можуть використовуватись для оптимізації умов вирощування монокристалів KDP з водних розчинів.