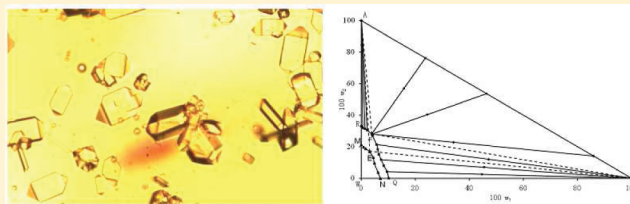


Solid–Liquid Phase Equilibrium for the Ternary System $K_2SO_4 + KH_2PO_4 + H_2O$ at (298.15 and 333.15) K

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ABSTRACT: The ternary system of $K_2SO_4 + KH_2PO_4 + H_2O$ at (298.15 and 333.15) K was investigated by the method of isothermal solution saturation and moist residues. Thus the solubility data of the system were obtained, and phase diagrams of $K_2SO_4 + KH_2PO_4 + H_2O$ at (298.15 and 333.15) K were constructed on the basis of the solubility data. The solid phase in the system mentioned above was also identified. The crystallization field of potassium sulfate and potassium dihydrogen phosphate (KDP) were determined, and the crystallization field of potassium sulfate was larger than that of potassium dihydrogen phosphate. The density of saturated solutions for the systems studied at (298.15 and 333.15) K was also measured. The solubility data, density, and the phase equilibrium diagrams for the ternary system can provide the fundamental basis for the preparation of potassium dihydrogen phosphate in potassium sulfate and potassium dihydrogen phosphate aqueous mixtures.



INTRODUCTION

Potassium dihydrogen phosphate (KDP) is an important industrial material and compound fertilizer which is widely used in industrial and agricultural fields. However, the KH_2PO_4 solution produced often contains many impurities, such as sulfate ions.^{1,2} To produce pure KH_2PO_4 , the crystallization process is a crucial step in producing KDP.¹

It is well-known that the solubility of potassium sulfate in water is smaller than that of KDP. The concentration of potassium sulfate reaches saturation first, and the potassium sulfate can crystallize from the aqueous solution containing K^+ , SO_4^{2-} , and $H_2PO_4^-$ ions, during the crystallization process. Therefore, KH_2PO_4 product attained after cooling crystallization usually contains a small quantity of potassium sulfate. Thus, the purity,^{3,4,6} crystal shape,^{5,6} and growth rate^{7–9} of KH_2PO_4 crystal were obviously influenced. Hence, to get the pure KDP, the concentration of the P_2O_5 and SO_4^{2-} in the solution must be controlled. From the phase equilibrium, the appropriate concentration of the P_2O_5 and SO_4^{2-} can be obtained for the crystallization process. The phase equilibrium of the $K_2SO_4 + KH_2PO_4 + H_2O$ system is of vital importance in crystallization process. However, the completely phase equilibrium data of $K_2SO_4 + KH_2PO_4 + H_2O$ system at (298.15 and 333.15) K has not been reported yet.

EXPERIMENTAL SECTION

Materials. Potassium dihydrogen phosphate (KH_2PO_4 , 0.995 mass fraction) was obtained from Tianjin Bodi Chemical Holding Co. Ltd., China. Potassium sulfate (K_2SO_4 , 0.990 mass fraction) was bought from Kermel Chemical Reagent Co. Ltd., China. Doubly deionized water (electrical conductivity $\leq 1 \cdot 10^{-4} \text{ S} \cdot \text{m}^{-1}$) was employed in this work.

Instrument. An HH-601 type super constant-temperature water bath (temperature range (278.15 to 368.15) K) was used for the phase equilibrium measurement with which the temperature could be controlled to ± 0.1 K. The water bath was produced by Jintan Medical Instrument Corporation, China. A Philips X'Pert Pro MPD X-ray diffraction analyzer was used for solid-phase X-ray analysis.

Experimental Method. The solubility was determined by the method of isothermal solution saturation.^{10–12} At a certain temperature, when pure KH_2PO_4 is put in the saturated solution of pure K_2SO_4 , the solubility of K_2SO_4 will decrease, because of the same ion effect. The solubility of K_2SO_4 will remain unchanged until KH_2PO_4 cannot be dissolved any more. The solution in which K_2SO_4 and KH_2PO_4 are both saturated is known as the cosaturation solution. The composition of the solution at this temperature and pressure is invariable, so this point is named as the invariant point in the phase diagrams. Although KH_2PO_4 exists in the solution, only K_2SO_4 is saturated in the water before the solution achieves cosaturation. In this way, we get a series of points that represent the solubility of K_2SO_4 in water. Similarly, points are attained representing the solubility of KH_2PO_4 in water.

It is difficult and cumbersome to separate crystals from mother liquor completely. So, the extrapolation, which is determined by Schreinemaker's method of wet residues,^{12–16} is used to determine the composition of the solid phase indirectly.

As is well-known, the compound point must be on the tie line joining the composition of the pure solid and the saturated liquid in equilibrium. The composition of wet residues which indicates that a little mother liquor adheres to the crystals can

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be obtained on the tie line mentioned above, undoubtedly. A straight line drawn through a pair of points representing saturated liquid and wet residues on a phase diagram is a segment of the tie line and therefore passes through the composition of the pure solid. In this way, many straight lines are drawn; some have a common intersection point that is the composition of the pure solid phase.

Experimental Procedure. A known mass of potassium sulfate, KDP, and doubly deionized water was loaded into a clean three-mouth bottle with a round bottom. Then, the bottle was placed in the constant-temperature bath. The complex was stirred continuously with a Teflon-coated magnetic stirring bar, and the actual temperature of the complex was monitored by a mercury thermometer (uncertainty, ± 0.1 K). In this experiments, when the concentrations of the P_2O_5 and SO_4^{2-} in the solution both remain constant after 3 h, each run reached equilibrium; for caution's sake, all of the systems were always stirred for at least 5 h. When a run achieved equilibrium, the liquid phase—saturated solution—was treated as follows: it was removed out by a straw whose temperature was about (298.15 or 333.15) K. The liquid phase was weighed before it was placed into a volumetric flask with a capacity of 100 mL and then diluted with deionized water immediately. At the same time, a part of the liquid phase was placed into a gravity bottle to measure the density. The wet solid was taken out by a scoop to weigh it. Afterwards it was dissolved by deionized water, transferred the solution to a volumetric flask with a capacity of 100 mL, and diluted with deionized water. Finally, these samples were quantitatively analyzed.

Analysis. The P_2O_5 concentration was measured by the quinoline phosphomolybdate gravimetric method.¹⁷ The average relative deviation of the determination was less than 0.3 % by this method. The sulfate radical ion concentration was determined by means of barium sulfate turbidimetry.¹⁸ The mean relative deviation of the determination was less than 0.5 %. The density was measured with Ostwald–Sprengel type pycnometers with a bulb volume of 10 cm³ and an internal capillary diameter of about 1 mm.¹⁹ The absolute uncertainties in the density measurements were estimated to be within 0.0002 g·cm⁻³. The average value of three measurements was considered as the final value of each analysis.

RESULTS AND DISCUSSION

The phase equilibrium experimental results of solubility measured for the ternary $K_2SO_4 + KH_2PO_4 + H_2O$ system at (283.15 and 333.15) K are shown in Tables 1 and 2, respectively. The density for the system is shown in Table 3. The ternary system phase diagram is given in Figure 1.

In the phase diagram as shown in Figure 1, W, A, and B represent H_2O , pure solid of KH_2PO_4 , and K_2SO_4 , respectively; E (F) is an invariant point at 283.15 K (333.15 K), which represents the cosaturated solution of K_2SO_4 and KH_2PO_4 ; M (R) represents the solubility of KH_2PO_4 in water at 283.15 K (333.15 K), and N (Q) represents that of K_2SO_4 in water at 283.15 K (333.15 K). Curves ME or RF, at (283.15 or 333.15) K, indicate that KDP has been saturated in the water. Similarly, NE and QF are also saturation curves corresponding with the solid-phase potassium sulfate of at (283.15 and 333.15) K, respectively.

As shown in Figure 1, along the solubility curve RF, linking the component points of the liquid phase and moist solid phase and an extension thereof, the point of intersection of these tie-lines is approximately the solid-phase component for the

Table 1. Mass Fraction Solubility of the Ternary $K_2SO_4 + KH_2PO_4 + H_2O$ System at 298.15 K^a

| no. | liquid phase | | moist solid phase | | equilibrium solid phase |
|-------|--------------|-----------|-------------------|-----------|-------------------------|
| | 100 w_1 | 100 w_2 | 100 w_1 | 100 w_2 | |
| 1, N | 7.16 | 0.00 | | | S |
| 2 | 6.28 | 3.67 | 76.00 | 0.94 | S |
| 3 | 4.92 | 9.64 | 75.00 | 2.46 | S |
| 4 | 4.45 | 13.24 | 69.90 | 3.99 | S |
| 5 | 3.22 | 17.00 | 1.70 | 73.22 | S+P |
| 6, E | 3.20 | 17.02 | 25.18 | 17.09 | S+P |
| 7 | 3.14 | 17.06 | 14.42 | 50.19 | S+P |
| 8 | 1.71 | 18.75 | 0.66 | 74.95 | P |
| 9 | 0.90 | 19.69 | 0.43 | 73.96 | P |
| 10, M | 0.00 | 21.44 | | | P |

^a w_1 , mass fraction of K_2SO_4 ; w_2 , mass fraction of KH_2PO_4 ; S, K_2SO_4 ; P, KH_2PO_4 .

Table 2. Mass Fraction Solubility of the Ternary $K_2SO_4 + KH_2PO_4 + H_2O$ System at 333.15 K^a

| no. | liquid phase | | moist solid phase | | equilibrium solid phase |
|-------|--------------|-----------|-------------------|-----------|-------------------------|
| | 100 w_1 | 100 w_2 | 100 w_1 | 100 w_2 | |
| 1, Q | 10.22 | 0.00 | | | S |
| 2 | 9.53 | 4.29 | 44.61 | 2.63 | S |
| 3 | 8.38 | 8.07 | 43.24 | 5.01 | S |
| 4 | 7.41 | 11.79 | 45.40 | 6.95 | S |
| 5 | 6.62 | 15.04 | 47.79 | 8.40 | S |
| 6 | 6.11 | 18.38 | 41.22 | 11.56 | S |
| 7 | 5.75 | 21.41 | 47.21 | 12.00 | S |
| 8 | 4.19 | 26.97 | 68.00 | 9.02 | S |
| 9 | 4.03 | 27.97 | 34.03 | 22.89 | S+P |
| 10, F | 3.99 | 28.09 | 24.45 | 40.43 | S+P |
| 11 | 3.96 | 28.18 | 15.81 | 56.97 | S+P |
| 12 | 2.14 | 30.49 | 0.59 | 84.10 | P |
| 13 | 1.32 | 31.30 | 0.33 | 85.78 | P |
| 14 | 0.55 | 31.99 | 0.13 | 84.37 | P |
| 15, R | 0.00 | 33.03 | | | P |

^a w_1 , w_2 , S, P, have the same meaning as described in Table 1.

Table 3. Density ρ for the Ternary $K_2SO_4 + KH_2PO_4 + H_2O$ System at (298.15 and 333.15) K

| no. ^a | $10^{-3} \rho / (\text{kg} \cdot \text{m}^{-3})$ | | |
|------------------|--|------------------|--------------|
| | T/K = 298.15 | no. ^a | T/K = 333.15 |
| 1, N | 1.0433 | 1, Q | 1.0587 |
| 2 | 1.0528 | 2 | 1.0673 |
| 3 | 1.0674 | 3 | 1.0754 |
| 4 | 1.0781 | 4 | 1.0839 |
| 5 | 1.0870 | 5 | 1.0930 |
| 6, E | 1.0869 | 6 | 1.1027 |
| 7 | 1.0943 | 7 | 1.1108 |
| 8 | 1.0797 | 8 | 1.1278 |
| 9 | 1.0763 | 9 | 1.1328 |
| 10, M | 1.0802 | 10, F | 1.1318 |
| | | 11 | 1.1321 |
| | | 12 | 1.1271 |
| | | 13 | 1.1245 |
| | | 14 | 1.1222 |
| | | 15, R | 1.1210 |

^aNumbers in this table correspond to Tables 1 and 2.

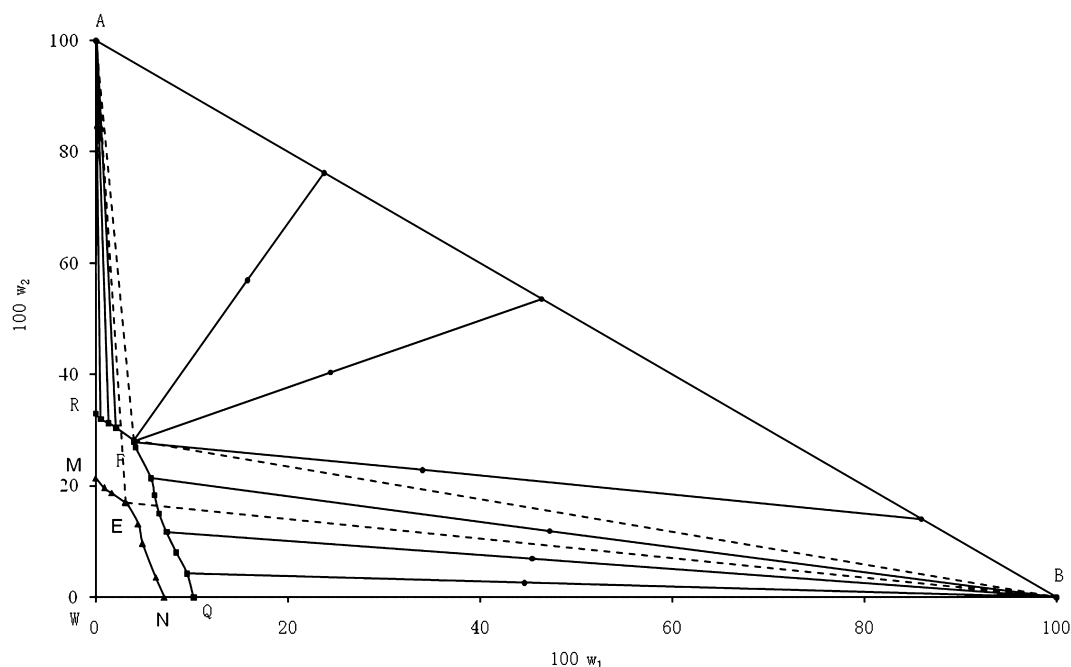


Figure 1. Phase diagram for the ternary $\text{K}_2\text{SO}_4 + \text{KH}_2\text{PO}_4 + \text{H}_2\text{O}$ system at (298.15 and 333.15) K. \blacktriangle , 298.15 K; \blacksquare , 333.15 K; \bullet , moist solid phase composition at 333.15 K; W, H_2O ; A, pure solid of KH_2PO_4 ; B, pure solid of K_2SO_4 ; E, cosaturated point of K_2SO_4 and KH_2PO_4 ; M, solubility of KH_2PO_4 in water; N, solubility of K_2SO_4 in water; F, cosaturated point of $\text{K}_2\text{SO}_4 + \text{KH}_2\text{PO}_4$; R, solubility of KH_2PO_4 in water; Q, solubility of K_2SO_4 in water.

KH_2PO_4 .¹⁴ So, in the same way, along the solubility curve QF, linking the component points of the liquid phase and moist solid phase and an extension thereof, the point of intersection of these tie-lines is approximately solid-phase component for the K_2SO_4 .

It can be seen from Figure 1 that WMN and WRQ are unsaturated regions at (298.15 and 333.15) K, respectively; MAE and RAF are crystalline regions of the pure KDP; NBE and QBF are crystalline regions of the pure potassium sulfate. AEB and AFB are crystalline regions of the $\text{K}_2\text{SO}_4 + \text{KH}_2\text{PO}_4$ mixture. This diagram further illustrates that the temperature can influence the equilibrium of the ternary system. Increasing the temperature from (298.15 to 333.15) K, the unsaturated region becomes larger apparently, and the invariant point moves upward from point E to F, because of that, at (298.15 and 333.15) K, the solubility of KDP and potassium sulfate in water increase. Both at (298.15 and 333.15) K, crystalline regions of the pure potassium sulfate are larger than that of the pure KDP.

Table 3 indicates that the densities of the saturated solutions gradually increase, at first, and then decrease with increasing P_2O_5 concentration.

CONCLUSION

The solubility data, density, and phase equilibrium of the ternary system of $\text{K}_2\text{SO}_4 + \text{KH}_2\text{PO}_4 + \text{H}_2\text{O}$ at (298.15 and 333.15) K were obtained. The phase diagrams of that system were constructed on the basis of the solubility data. The crystalline regions of potassium sulfate and KDP were determined, and the crystallization fields of potassium sulfate were both larger than that of KDP at (298.15 and 333.15) K. Each phase diagram has only one invariant point (point E or F).

The solubility data, density, and the phase equilibrium diagrams for the ternary system can provide the fundamental

basis for the preparation of KDP in potassium sulfate and KDP aqueous mixtures.

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Notes

The authors declare no competing financial interest.

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