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Research Article

Solid-Liquid Phase Equilibria for the Ternary System $KNO_3 + KH_2PO_4 + H_2O$ at 283.15, 298.15, and 313.15 K

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The solid-liquid phase equilibria of the ternary system $KNO_3 + KH_2PO_4 + H_2O$ at the temperatures of 283.15, 298.15, and 313.15 K and the pressure of 0.1 MPa are researched by isothermal solution saturation. The equilibria solid phases are researched by Schreinemakers method (wet residues). The solubility data are determined. Based on these data, the phase diagrams and the crystalline areas are determined. The phase equilibria at different temperatures are compared and discussed. All results can provide basic data support for crystallization and further researches.

1. Introduction

Salt-water phase equilibria, an important predicting implement to apply for representing the thermodynamic behavior, play a very great guiding role for the relevant process [1, 2]. KNO_3 is a source of potassium and soluble nitrogen, both of which are vital plant nutrients, and this material is widely used in agricultural and industrial fields [3]. KH_2PO_4, as an important industrial material and compound fertilizer, is widely used in agricultural, chemical, pharmaceutical, and food industry [4, 5].

The solubility data of the ternary system $KNO_3 + KH_2PO_4 + H_2O$ can be discovered in previous researches [6, 7] and were reported about 40–80 years ago. In their experiments, different experimental ways, different apparatuses, and different analytical ways were used to obtain data. However, the details of these experiments and no more recent data are not discovered for the ternary system. As we all know, experimental conditions and analytical ways have been gradually improved. Therefore, it is essential to supply more data. At the same time, the data presented are far from enough, so an extensive research at other temperatures needs to be done. The complete phase equilibria data of the $KNO_3 + KH_2PO_4 + H_2O$ system at 283.15 K and 313.15 K have not been reported yet. The thesis could help fill in the blank of data in the research, and new experimental data are useful for scholars and engineers to cope with the problem of obtaining and storage of manures containing potassium nitrate and phosphates. Additionally, all results can provide basic data support for industry and further theoretical studies.

2. Methodology

2.1. Materials and Apparatus. Potassium dihydrogen phosphate (KH_2PO_4, ≥0.995 mass fraction) and potassium nitrate (KNO_3, ≥0.995 mass fraction) are from Tianjin Bodi Chemical Holding Co., Ltd., China. Doubly deionized water (electrical conductivity $\leq 1 \cdot 10^{-4}\ S \cdot m^{-1}$) is employed in the thesis. The purities and sources of the chemicals are listed in Table 1.

A HZS-HA thermostatic vibrator is used to measure phase equilibria and made in Donglian Electronic & Technology Development Co., Ltd., Beijing, China.

2.2. Experimental Method. The method, isothermal solution saturation [8–10], is employed for determining the solubility data. The famous Schreinemakers method (wet residues [11–13]) is applied to analyze the composition of the equilibria solid phase.

Table 1: Purities and suppliers of chemicals.

Chemical	Mass fraction purity	CAS number	Source
KH_2PO_4	≥0.995	7778-77-0	Tianjin Bodi Chemical Holding Co., Ltd., China
KNO_3	≥0.995	7757-79-1	Tianjin Bodi Chemical Holding Co., Ltd., China

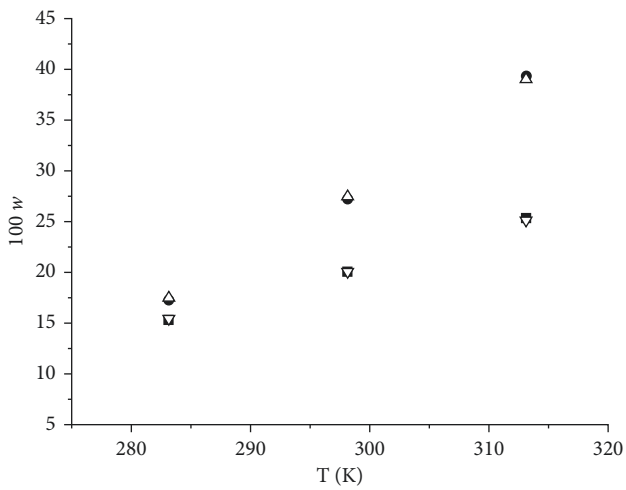

Figure 1: Solubility for KH_2PO_4 or KNO_3 in pure water at 283.15, 298.15, and 313.15 K. ▽ literary solubility of KH_2PO_4 in water [18]; ■ experimental solubility of KH_2PO_4 in water; △ literary solubility of KNO_3 in water [10]; ● experimental solubility of KNO_3 in water.

According to a fixed ratio and making sure that one of the components is in excess, the experimental components are added into a series of conical flasks (250 mL) gradually, and the sealed flask is placed into the thermostatic vibrator. The vibrator oscillates continuously at the specific temperatures: 283.15 K, 298.15 K, and 313.15 K. In a pre-experiment, the liquid phase of the samples is analyzed at every 2 h. It is shown that the phase equilibria are reached in 10 h. After equilibria, the oscillation is stopped and the system is allowed to stand for 3 h to make sure that all the suspended crystals settle. The liquid phase and wet residues are transferred to 250 mL volumetric flasks, respectively. Finally, the samples are quantitatively analyzed by chemical ways.

More details of the experimental method and the procedure of the preparation, collection, and transfer of samples are depicted in the previous theses [8, 10].

2.3. Analysis. The concentration of $H_2PO_4^-$ is determined by the quinoline phosphomolybdate gravimetric way [14] with a relative standard uncertainty of 0.01. The potassium ion is analyzed by a gravimetric way with sodium tetraphenylboron [15–17], and the relative standard uncertainty is 0.01. The experimental results are achieved from the average value of three parallel measurements.

3. Results and Discussion

In Figure 1, the experimental data are compared with the literature [10, 18] and it is discovered that the experimental values

Table 2: Mass fraction solubility of the ternary KNO_3 (1) + KH_2PO_4 (2) + H_2O system at the temperatures of 283.15, 298.15, and 313.15 K and the pressure of 0.1 MPa[a].

Number	Composition of liquid phase, 100 w[b]		Composition of wet residue phase, 100 w		Equilibrium solid phase
	100 w_1	100 w_2	100 w_1	100 w_2	
283.15 K					
1	17.29	0.00	ND[c]	ND	KNO_3
2	16.43	1.94	47.40	1.35	KNO_3
3	15.46	3.95	48.59	2.53	KNO_3
4	14.73	5.81	49.91	3.54	KNO_3
5	13.92	7.92	48.15	4.89	KNO_3
6	13.34	9.33	49.28	16.68	$KH_2PO_4 + KNO_3$
7	13.34	9.33	14.92	44.48	$KH_2PO_4 + KNO_3$
8	11.85	9.94	7.27	44.99	KH_2PO_4
9	9.72	10.87	5.83	46.93	KH_2PO_4
10	7.00	11.98	4.45	44.73	KH_2PO_4
11	4.70	12.89	3.13	42.97	KH_2PO_4
12	2.51	13.90	1.63	45.32	KH_2PO_4
13	0.00	15.35	ND	ND	KH_2PO_4
298.15 K					
1	0.00	20.05	ND	ND	KH_2PO_4
2	3.64	17.29	1.94	59.39	KH_2PO_4
3	7.52	15.19	3.76	58.47	KH_2PO_4
4	10.59	13.63	4.95	60.07	KH_2PO_4
5	14.60	11.91	6.83	58.97	KH_2PO_4
6	17.61	10.68	8.40	57.71	KH_2PO_4
7	20.41	9.68	10.09	55.69	KH_2PO_4
8	22.16	9.07	18.06	56.70	$KH_2PO_4 + KNO_3$
9	22.16	9.07	53.23	16.34	$KH_2PO_4 + KNO_3$
10	23.33	7.00	53.67	4.30	KNO_3
11	24.33	4.97	55.24	3.03	KNO_3
12	25.96	2.11	56.11	1.35	KNO_3
13	27.25	0.00	ND	ND	KNO_3
313.15 K					
1	39.30	0.00	ND	ND	KNO_3
2	37.37	2.53	60.69	1.68	KNO_3
3	34.86	5.46	59.12	3.54	KNO_3
4	33.22	7.50	55.24	18.96	$KH_2PO_4 + KNO_3$
5	33.22	7.50	29.03	43.56	$KH_2PO_4 + KNO_3$
6	31.14	8.42	17.18	49.62	KH_2PO_4
7	28.09	9.60	15.30	50.88	KH_2PO_4
8	25.40	10.56	14.61	48.53	KH_2PO_4
9	22.83	11.60	12.48	51.73	KH_2PO_4
10	19.95	12.85	11.54	49.62	KH_2PO_4
11	17.38	14.23	9.72	52.23	KH_2PO_4
12	14.55	15.75	8.09	53.33	KH_2PO_4
13	10.90	17.99	6.02	54.93	KH_2PO_4
14	7.31	20.09	3.95	56.95	KH_2PO_4
15	3.29	22.70	1.94	54.51	KH_2PO_4
16	0.00	25.32	ND	ND	KH_2PO_4

[a]Standard uncertainties $u(T) = 0.3$ K, $u_r(p) = 0.05$, $u_r(w_1) = 0.01$, and $u_r(w_2) = 0.01$. [b]w_1, mass fraction of KNO_3; w_2, mass fraction of KH_2PO_4; [c]ND, not determined.

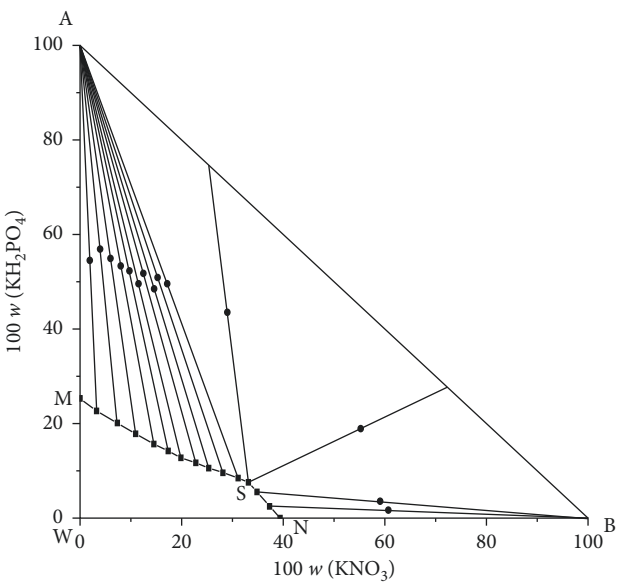

Figure 2: Equilibrium phase diagram of the ternary system $KH_2PO_4 + KNO_3 + H_2O$ at 313.15 K. ▪ equilibrium liquid phase composition; ● moist solid phase composition; A, pure solid of KH_2PO_4; B, pure solid of KNO_3; W, water; M, solubility of KH_2PO_4 in water; N, solubility of KNO_3 in water; S, cosaturated point of KH_2PO_4 and KNO_3.

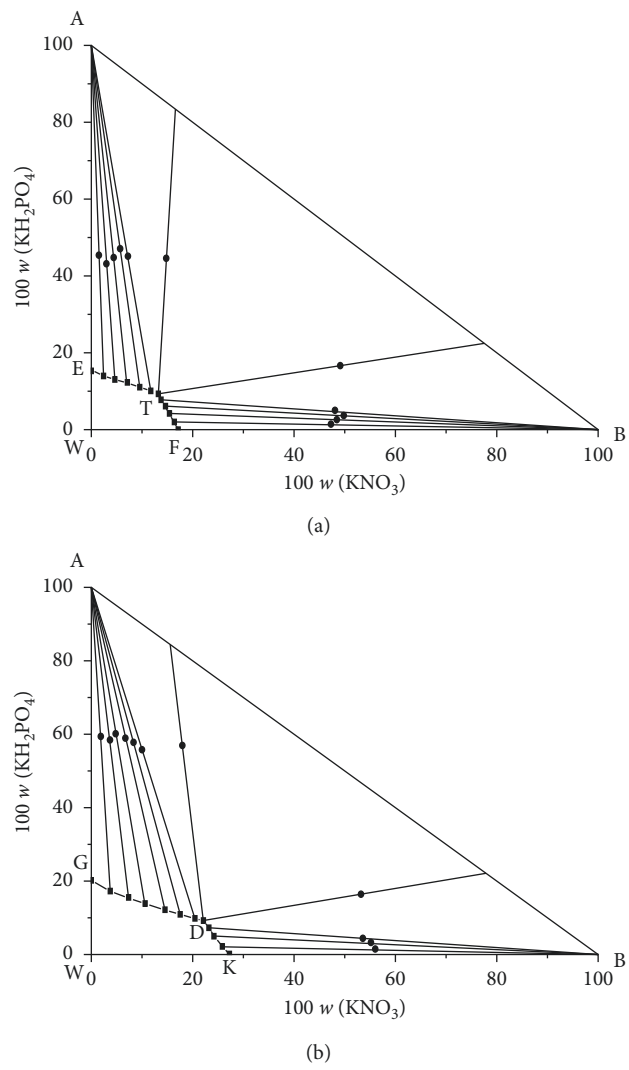

Figure 3: Equilibrium phase diagram of the ternary system $KH_2PO_4 + KNO_3 + H_2O$ at (a) 283.15 and (b) 298.15 K. ▪ equilibrium liquid phase composition; ● moist solid phase composition; A, pure solid of KH_2PO_4; B, pure solid of KNO_3; W, water; E and G, solubility of KH_2PO_4 in water; F and K, solubility of KNO_3 in water; T and D, cosaturated point of KNO_3 and KH_2PO_4.

are in good agreement with the literature, which illustrates that experimental ways and devices are feasible in this thesis.

The phase equilibria data are listed in Table 2. Based on these data, the ternary phase diagram is illustrated in Figure 2 and the phase diagrams at other temperatures are illustrated in Figure 3 and are similar to that in Figure 2.

In Figure 2, A, B, and W represent solid KH_2PO_4, solid KNO_3, and H_2O, respectively. Point S, an invariant point at 313.15 K, reflects the cosaturated solution of KNO_3 and KH_2PO_4. M represents the solubility of KH_2PO_4 in water at 313.15 K. N represents the solubility of KNO_3 in water at 313.15 K. The saturated liquid line MSN consists of two branches. MS corresponds to the saturated KH_2PO_4 solution and visualizes changes of KH_2PO_4 concentration with the KNO_3 concentration rising in the equilibria solution. SN corresponds to the saturated KNO_3 solution and indicates changes of KNO_3 concentration with the KH_2PO_4 concentration rising.

As indicated in Figures 2 and 3, along the curve MS, the composition points of wet residue phase and liquid phase are connected and then extended, and the intersection of the lines is the solid phase component for KH_2PO_4. The same is used for determining the equilibria solid phase component of SN, that is, KNO_3. Similarly, the equilibria solid phases of A and B at 298.15 K are KH_2PO_4 and KNO_3, respectively; the equilibria solid phases of A and B at 283.15 K are same. Consequently, the ternary system is a simple eutectic type, and neither double salt nor solid solution is formed at the investigated temperature range. In Figure 2, WMSN denotes the unsaturated region at 313.15 K. AMS represents the crystalline region of KH_2PO_4, while NSB denotes the crystalline region of KNO_3. Zone ASB denotes the mixed crystalline region of $KNO_3 + KH_2PO_4$. The crystalline region of KH_2PO_4 is larger than the crystalline region of KNO_3 at each researched temperature.

In Figure 4, the literature [7] and experiment data at 298.15 K are compared. A good resemblance is obtained between the literature and experimental data. But the values in the literature show a little inconsistency when compared with our data. After the original literature, maybe the difference is cause by different shaking time and analytical methods. A comparison among the phase equilibria of $KNO_3 + KH_2PO_4 + H_2O$ at 283.15, 298.15, and 313.15 K are shown in Figure 5, which further elucidates that temperatures can affect the equilibria. Raising from 283.15 K to 313.15 K, the unsaturated area becomes larger apparently, and the crystalline region of KH_2PO_4 becomes larger, while the crystalline region of KNO_3 becomes smaller, which illustrates that it is feasible to purify the mixed solution by

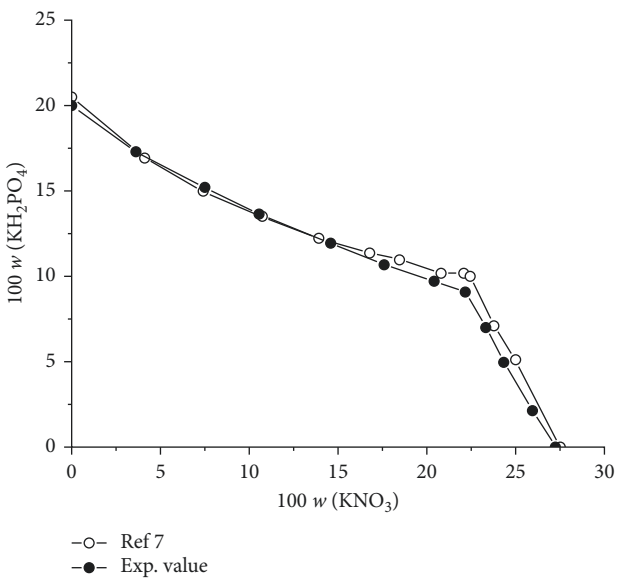

Figure 4: Solubility for the ternary system $KH_2PO_4 + KNO_3 + H_2O$ at 298.15 K.

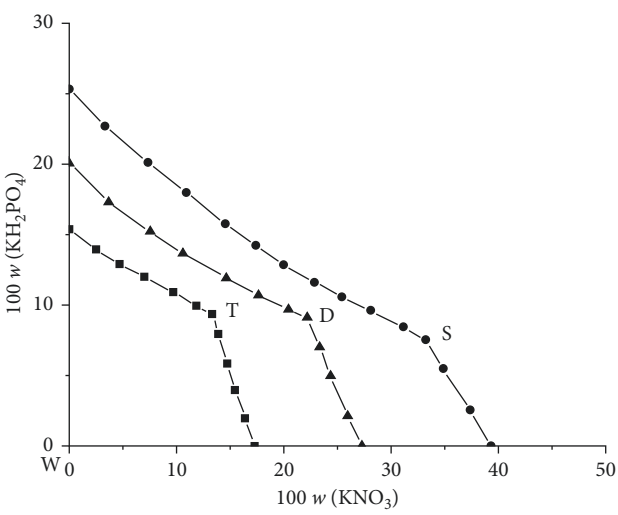

Figure 5: Solubility for the ternary system $KH_2PO_4 + KNO_3 + H_2O$ at 283.15, 298.15, and 313.15 K. ■ 283.15 K; ▲ 298.15 K; ● 313.15 K; W, T, D, and S have the same meaning as described in Figures 2 and 3.

changing crystalline temperature. The invariant point moves right from point T, to D, to S, which elucidates that the salting-out effect of KH_2PO_4 on KNO_3 does not change significantly. The equilibria solid phase remains the same, and only anhydrous potassium nitrate and potassium dihydrogen phosphate exist as solid phases.

The differences in KNO_3 and KH_2PO_4 solubility between the aqueous solutions and invariant points are presented in Figure 6. The differences in KNO_3 solubility between the aqueous solutions and invariant points are 3.95%, 5.09%, and 6.08% at 283.15, 298.15, and 313.15 K, respectively, which elucidates KH_2PO_4 has a salting-out effect on KNO_3. The differences in KH_2PO_4 solubility between the aqueous solutions and invariant points are 6.02%, 10.98%, and 17.82% at

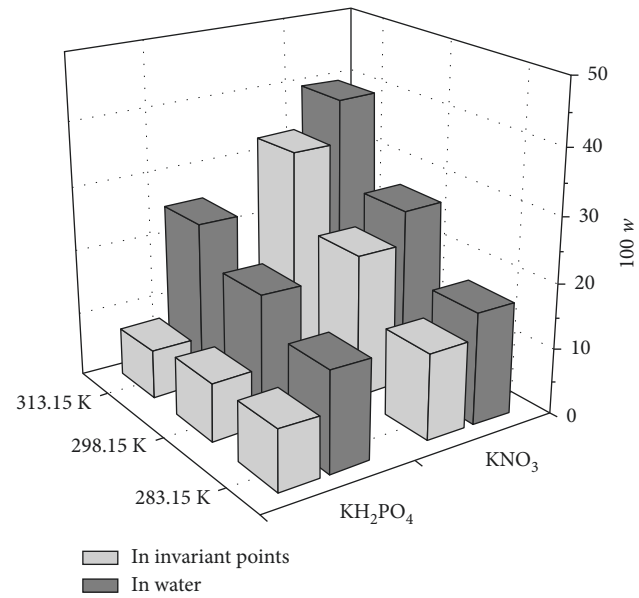

Figure 6: Comparison of the KH_2PO_4 and KNO_3 solubility in aqueous solutions and at cosaturated points T, D, and S.

283.15, 298.15, and 313.15 K, respectively, which elucidates that KNO_3 has a salting-out effect on KH_2PO_4 and the effect is stronger at higher temperatures. The salting-out effect of KNO_3 on KH_2PO_4 is stronger than that of KH2PO4 on KNO_3.

4. Conclusions

The solid -liquid phase equilibria of $KNO_3 + KH_2PO_4 + H_2O$ at 283.15, 298.15, and 313.15 K are researched. The solubility data are obtained. Based on these data, the phase diagrams and the crystalline areas of both solid phases are determined. There are two crystalline areas, one invariant point and two univariant curves. The ternary system is a simple eutectic type, and the crystalline area of KH_2PO_4 is larger than the crystalline area of KNO_3 at each researched temperature. Raising from 283.15 K to 313.15 K, the equilibria solid phase remains unchanged, and the crystalline area of KH_2PO_4 expands, while the crystalline area of KNO_3 decreases. KNO_3 has a salting-out effect on KH_2PO_4, and the effect is stronger at higher temperatures. The salting-out effect of KNO_3 on KH_2PO_4 is stronger than that of KH_2PO_4 on KNO_3. All results can provide basic data support for separation and further researches.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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