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Solubility and Critical Relative Humidity of the System ($KH_2PO_4 + K_2HPO_4 + H_2O$) at 298.15 K

Kalina D. Kamburova[†] **and Plamen P. Kirilov***

Department of Inorganic Chemical Technologies, University of Chemical Technology and Metallurgy, Sofia, Bulgaria

The critical relative humidity (CRH) and creeping crystallization of saturated solutions of the system ($KH_2PO_4 + K_2HPO_4 + H_2O$) at 298.15 K have been measured. The CRH was measured by a high-precision laboratory water activity meter. The creeping crystallization and the behavior of the solutions were tested at room conditions during a period of 25 days of exposure. The most suitable stock solution for producing foliar phosphorus−potassium (PK) and nitrogen−phosphorus−potassium (NPK) fertilizers from the viewpoint of these two properties was determined.

Introduction

Recently, there has been an enormous increase in the production and marketing of a variety of foliar fertilizers. The reasons for this are the many benefits of foliar feeding of plants. Foliar feeding is an effective method for correcting soil deficiencies and overcoming the soil's inability to transfer nutrients to the plant.

The quality of the liquid fertilizers and the effectiveness of foliar applied nutrients are determined by many factors: solubility, density, pH, salt index, viscosity, electrical conductivity, vapor pressure, surface tension, corrosion activity, temperature of crystallization, stability, and so forth.[1−4] Aqueous solutions of the mixtures of KH_2PO_4 and K_2HPO_4 have many benefits as foliar fertilizers, and they are very suitable for this purpose. The benefits stated until now are the following: high solubility and high concentration of nutrients,[5,6] very low salt index,[7−9] inhibition of the development of powdery mildew fungus,[10] and high buffer capacity.[11]

Density and water activity of diluted solutions in the ternary system ($KH_2PO_4 + K_2HPO_4 + H_2O$) at 298.15 K have been measured by Kabiri-Badr and Zafarani-Moattar.[12] However, there are no data for the saturated solutions in the above-mentioned system.

Selected properties, solubility, density, pH, electrical conductivity, and corrosion activity, of the system ($KH_2PO_4 + K_2HPO_4 + H_2O$) saturated at 298.15 K, have been investigated and presented in our previous paper.[13] Two additional properties of this system, critical relative humidity (CRH) and creeping crystallization, are objectives of the present supplementary study. The aim of all of these investigations is to determine the most appropriate composition of the solution suitable for foliar fertilization from the viewpoint of its physicochemical properties.

One of the main factors related to foliar fertilizers is the length of time the nutrient remains dissolved in the solution on the leaf's surface. Some time is necessary for the absorption of the nutrients and their penetration into the leaves. This property of a foliar fertilizer can be qualified and quantified by measuring of the CRH.

The CRH of a salt is defined as the relative humidity (RH) of the surrounding atmosphere (at a certain temperature) above which the material begins to absorb moisture from the atmosphere and below which it will not absorb atmospheric moisture. At the CRH the salt and its saturated solution are in equilibrium. The RH is the ratio (expressed as a percentage) of the partial pressure of the water vapor actually present to the partial pressure of water present at saturation in air at the same temperature. The salt solutions have lower vapor pressure than pure water.

All water-soluble salts and mixtures have a characteristic critical humidity. This is a specific and definite physical property of any pure compound. The value of CRH decreases with increasing temperature and is significantly influenced by the number of species in solution. Compounds exhibiting poor water solubility typically have high RH values, and vice versa, as solubility increases, RH decreases.

For a solid fertilizer, a relatively high CRH is an advantage because such a material can be exposed and handled under more humid atmospheric conditions without the absorption of moisture that might promote caking. For a foliar fertilizer it is just the opposite: a relative low CRH is an advantage because the nutrients will remain dissolved for a long time on the leaves' surface and will be absorbed from them. Particularly important in mixed fertilizers is the fact that combinations of salts have lower critical values, that is, they are more hygroscopic than any of the components taken singly (except in a few cases of double salt formation).

Numerous methods for determination of CRH have been reported. A short description of them was given in Greenspan.[14] A new method has been developed recently to measure the RH by Fourier transform infrared (FTIR) spectroscopy.[15]

The International Organization of Legal Metrology (OIML) recommended a set of selected hydrostatic solutions—saturated solutions of specified salts with an excess of the salt to ensure saturation—whose RH values at a specific temperature correspond to fixed points of the scale of RH.[16]

The CRH of pure fertilizer compounds and some binary mixtures have been determined, first by Edgar and Swan[17] and later by Adams and Merz[18] and Merz et al.[19] Young[20] has presented the RH for 38 saturated salt solutions and listed details for salts which are recommended as suitable for humidity

* Corresponding author. E-mail: p_kirilov@uctm.edu.
[†] E-mail: kalina.kamburova@gmail.com.

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Table 1. Composition, ω, and Critical Relative Humidity, CRH, in the System ($KH_2PO_4 + K_2HPO_4 + H_2O$) at 298.15 K[a]

no.	K/P	$\omega(KH_2PO_4)_s$	$\omega(K_2HPO_4)_s$	$\omega(K_xH_yPO_4)_{aq}$	$\omega(P_2O_5)_{aq}$	$\omega(K_2O)_{aq}$	$\omega(PK)_{aq}$	CRH/%
1	0.663	100		20.12	10.49	6.96	17.45	95.6
2	0.7	93.12	6.98	20.73	11.43	8.00	18.43	95.1
3	0.8	75.13	24.87	25.84	12.74	10.12	22.86	94.2
4	0.9	58.56	41.44	32.49	15.41	13.86	29.27	91.3
5	1.0	43.18	56.82	42.37	19.35	19.35	38.70	86.4
6	1.1	28.93	71.07	55.42	24.41	26.85	51.26	72.8
7	1.2	15.63	84.37	66.88	28.44	34.14	62.58	43.0
8	1.3	3.24	96.79	63.41	26.07	33.89	59.96	43.9
9	1.327		100	62.37	25.42	33.73	59.15	44.4

[a] Legend. K/P, mass ratio $\omega(K_2O)/\omega(P_2O_5)$ in the solid mixture ($KH_2PO_4 + K_2HPO_4$); $\omega(KH_2PO_4)_s$, mass fraction of KH_2PO_4 in the solid mixture; $\omega(K_2HPO_4)_s$, mass fraction of K_2HPO_4 in the solid mixture; $\omega(K_xH_yPO_4)_{aq}$, mass fraction of ($KH_2PO_4 + K_2HPO_4$) in the solution; $\omega(P_2O_5)_{aq}$ and $\omega(K_2O)_{aq}$, mass fractions of P_2O_5 and K_2O in the solution; $\omega(PK)_{aq}$, total mass fraction of ($P_2O_5 + K_2O$) in the solution; CRH, critical relative humidity/%.

control. Greenspan has been made a critical review from the 21 separate investigations comprising 1106 individual measurements. Fits were made by the method of least-squares to regular polynomial equations. Equations and tables are presented along with the estimated uncertainties in the correlated results.

The data for the RH over saturated solutions of KH_2PO_4 and K_2HPO_4 are very scanty. Winston and Bates[21] reported the only value for K_2HPO_4 at 293 K, RH = 44.5 %, and values for the RH of KH_2PO_4 at various temperatures. The RH over saturated solution of KH_2PO_4 at 298 K is RH = 96.0 %. The data for the RH of KH_2PO_4 at various temperatures are given also from O'Brien.[22] The presented RH of this salt at 298 K is RH = 96.6 %.

The important role of the CRH of the foliar fertilizers and atmosphere humidity on the effectiveness of foliar feeding is stated by Schönherr and Luber.[23] They studied the effects of humidity, anions, and temperature on the cuticular penetration of different potassium salts. The temperature did not significantly influence the rates of penetration in the range of (283.15 to 298.15) K. From the investigated salts, KH_2PO_4 (CRH of 97 % at 293.15 K), KNO_3 (CRH of 95 %), KCl (CRH of 86 %), and K_2CO_3 (CRH of 44 %), K_2CO_3 is best suited for foliar applications as rates of penetration have been large at 50 % humidity and higher, while with the other salts humidity must be (90 to 100) % for maximum rates of penetration.

However, the CRH value alone gives no information as to how rapidly moisture will be absorbed or evaporated. The moisture absorption/evaporation rate is in many ways more important than the fact of its occurrence. It will be affected by: (1) the difference between the partial pressure of water vapor (RH) in the atmosphere and the vapor pressure of the saturated aqueous solutions (CRH), (2) the temperature, (3) the surface of material exposed, (4) the velocity of movement of moist air, and (5) a specific "reaction constant," characteristic of the solid itself.

The disadvantage of some liquid fertilizers is in their handling. Bottles containing concentrated solutions become sticky and difficult to open due to the crystallization of salts in the sealing mechanism. So another property of the liquid fertilizers, creeping crystallization, is important, too.

Only few studies on the creeping of saturated salt solutions have been presented. Washburn[24] tried various solutions and solid surfaces and noted the general nature of the phenomenon. The work of Washburn has been extended by Hazlehurst et al.,[25] and a few roughly quantitative results have been obtained. Creeping is supposed to occur when the solute is capable of displacing the solution from, and spreading over, the supporting surface. According to Shopova[26] the ability of the solute to creep depends from the value of the surface tension of the saturated solution. Solutions with surface tensions above (75 to 76) $mN \cdot m^{-1}$ can creep on glass dishes.

Experimental Section

KH_2PO_4 and K_2HPO_4 were supplied by Merck and were used without further purification.

Eight samples of saturated solutions at 298.15 K of KH_2PO_4, K_2HPO_4, and their mixtures with different ratios were prepared. Farther in the paper the mass ratio KH_2PO_4/K_2HPO_4 in the mixture will be presented by the K_2O/P_2O_5 mass ratio and will be signed shortly as K/P. It is the custom to sign the content of the primary nutrients P and K in a fertilizer as mass fractions of P_2O_5 and K_2O.

The CRH of the system ($KH_2PO_4 + K_2HPO_4 + H_2O$) was measured at 298.15 K. The experiments were provided on a laboratory water activity (a_w) meter (AquaLab 3TE, Decagon Devices, Inc., USA). The specifications of the instrument are the following: sensors, chilled-mirror condensation dewpoint and infrared sample surface temperature; accuracy, $\pm 0.003\ a_w$; range, 0.03 to 1.000 a_w; resolution, $\pm 0.001\ a_w$; repeatability, $\pm 0.001\ a_w$. By definition CRH = 100 % a_w.

Additional experiments have been made for determination of creeping crystallization and the behavior of the tested solutions. Samples of 20 mL of the saturated solutions were kept 25 days in open beakers ($V = 100$ mL and $d = 4.5$ cm) at room conditions ($T_{min} = 297.1$ K, $T_{max} = 300.9$ K, $RH_{min} = 37$ %, $RH_{max} = 71$ %). Each beaker with the sample was preweighed to an accuracy of 10^{-5} g and weighed periodically (every 5 days) during the experiment. Mass losses of the solutions were calculated by the equation:

$$\Delta m = \left[\frac{(m_0 - m_t)}{m_0}\right] \cdot 100\ \%$$

where m_0 is the initial mass of the sample and m_t is the mass of the sample after a given period of exposure.

After 25 days the creeping crystals on the wall of the beaker were scraped off, dried, and weighed. The extent of creeping was calculated as a ratio between the weight of the creeping salt and its initial weight in the solution sample.

Results and Discussion

In our previous paper[16] some properties, solubility, density, pH, electrical conductivity, and corrosion activity, of the system ($KH_2PO_4 + K_2HPO_4 + H_2O$) saturated at 298.15 K have been investigated, presented, and discussed. It was stated that according to the requirements to foliar liquid fertilizers the most suitable PK solution is that with a mass ratio K/P = 1.2. This solution is with the highest solubility and density

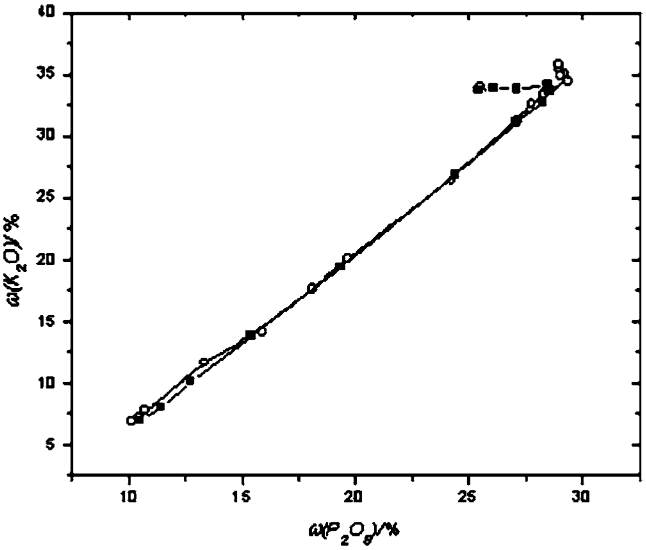

Figure 1. Solubility in the system $KH_2PO_4 + K_2HPO_4 + H_2O$ at 298.15 K. ■, this work; ○, Berg.[5]

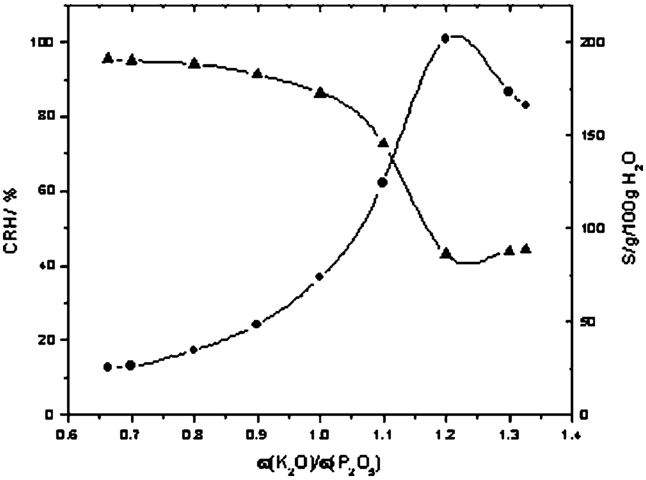

Figure 2. Plot of ●, solubility and ▲, CRH versus mass ratio K/P.

Table 2. Mass Losses of the Solutions, Δm, during Different Times of Exposure at Room Conditions

K/P days	0.663	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.327
5	21.37	20.86	19.59	17.83	13.69	6.53	1.27	1.33	1.69
10	47.12	47.47	42.37	37.19	26.94	12.08	2.38	2.49	2.94
15	70.93	70.81	61.52	50.38	34.54	15.08	2.81	2.92	3.22
20	79.89	77.55	69.34	55.73	38.19	16.89	3.09	3.19	3.47
25	79.90	77.61	69.38	55.87	38.28	16.95	3.18	3.25	3.54

and lowest electrical conductance and is practically noncorrosive.

The results for the composition of the saturated solutions and their CRH at 293.15 K are given in Table 1. The composition of the solutions was calculated from our experimental data on the solubility of the mixtures of KH_2PO_4 and K_2HPO_4 at different ratios in distilled water at 293.15 K. The solubility was determined with a precision of at least ± 0.0001 g/100 g H_2O and the concentration with ± 0.01 %.

A comparison between our data for the composition of the system ($KH_2PO_4 + K_2HPO_4 + H_2O$) and the data of Berg has been made. According to Wendrow and Kobe, the work of Berg was believed to be most accurate until 1954.

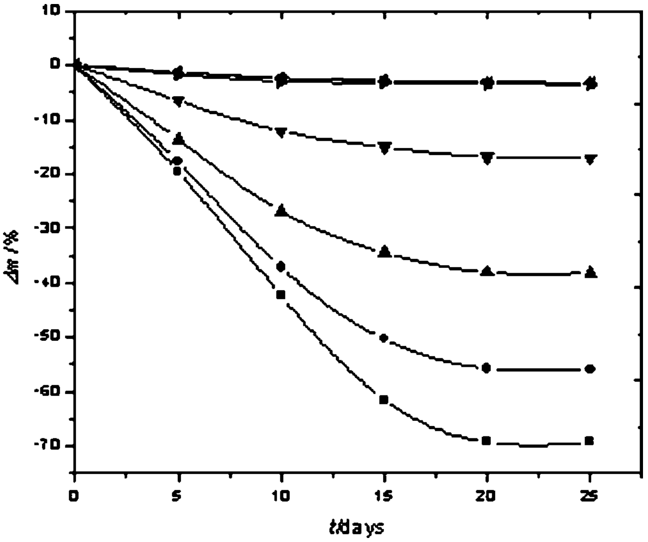

Figure 3. Plot of mass losses versus time corresponding to K/P ratios: ■, 0.663; ●, 0.7; ▲, 0.8; ▼, 0.9; ◆, 1.0; left-pointing triangle, 1.1; right-pointing triangle, 1.2; ●, 1.3; ★, 1.327.

As shown in Figure 1, our results are in good agreement with Berg's data. The maximum concentration of the nutrients in the solutions is reached at ratio K/P = 1.2.

The CRH of the saturated solution of K_2HPO_4 is approximately two times less than that of KH_2PO_4. Nevertheless the minimum value of the CRH in the system has been reached for a mixture of the said salts at definite ratio between them. An explanation of this phenomenon can be made from Figure 2, presenting the dependence of CRH and solubility from K/P ratio. It is seen that both curves have their extremes at one and the same value of K/P. CRH initially decreases slowly, but at P/K = 1.0 it begins to decrease sharply and reaches a minimum value 43 % at the ratio K/P = 1.2. The shape of the curve S versus K/P is reverse, and it also reaches an extreme maximum at the same ratio K/P = 1.2. It is obvious that the main factor affecting the value of CRH is the solubility, which in turn is a function of the K/P (KH_2PO_4/K_2HPO_4) ratio. According to thermodynamic principles, the CRH of electrolytes is closely related to their solubility.

The data for the mass losses of the solutions during their 25 day exposure at room conditions are given in Table 2. The change of the mass of the solutions at 5 day intervals is presented in Figure 3. The rate and the extent of vaporization decrease with increasing K/P ratio due to increasing the content of the more hygroscopic salt K_2HPO_4 in the solution. Solutions with K/P = 1.2, 1.3, and 1.327 with the lowest values of CRH do not change their masses significantly. These solutions can remain for a long time at ambient conditions without vaporization.

Creeping crystallization was observed only for the solutions with a high rate and extent of vaporization, that is, those with ratios K/P = 0.663, 0.7, and 0.8. The extents of creeping were very low: (8.2, 6.1, and 4.3) %, respectively. These solutions contain mainly the less soluble salt KH_2PO_4; they are diluted and respectively have high values of CRH. The rest of the solutions had no creeping crystallization.

At the end of this experiment on the bottom of most of the beakers a layer of crystals was formed. Only in the beakers with solutions with K/P = 1.2, 1.3, and 1.327 there were no crystals. The reason for this is that the dominant salt in these solutions is hygroscopic K_2HPO_4, with a very low CRH and rate of vaporization.

Conclusion

Aqueous solutions of the mixtures of KH_2PO_4 and K_2HPO_4 have many benefits as foliar fertilizers, and they are very suitable for this purpose. Our efforts are directed to determine the most appropriate composition of these solutions for foliar fertilization from the viewpoint of their physicochemical properties.

Solubility, density, pH, electrical conductivity, and corrosion activity of the system ($KH_2PO_4 + K_2HPO_4 + H_2O$) at 298.15 K have been measured in our previous study. It was stated that according to these properties the most suitable solution is that with a mass ratio K/P = 1.2.

In the present paper the results of supplementary investigations of two additional properties of this system, CRH and creeping crystallization, were presented. The composition of the saturated solutions at 298.15 K used for these studies has been compared with Berg's data for the same system, and a good agreement has been stated.

Solution with the lowest CRH (CRH = 43.0 %) is the most concentrated solution, that is, that with ratio K/P = 1.2 (15.63 % KH_2PO_4 and 84.37 % K_2HPO_4). This is in accordance with the thermodynamic principle that the CRH of electrolytes is closely related to their solubility.

This solution has a very low rate of vaporization, does not change the mass significantly, has no creeping crystallization, and does not form any crystals on the bottom of the beaker during 25 days of exposure at ambient conditions.

From the viewpoint of the previous and the present investigations on the physicochemical properties of the system ($KH_2PO_4 + K_2HPO_4 + H_2O$) at 298.15 K, the most suitable stock solution for producing foliar phosphorus−potassium (PK) and nitrogen−phosphorus−potassium (NPK) fertilizers is that with mass ratio $K_2O/P_2O_5 = 1.2$ (28.44 % P_2O_5 and 34.14 % K_2O).

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