Fluid Phase Equilibria 474 (2018) 131–140

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Solid-liquid phase equilibria in aqueous solutions of four common fertilizers at 303.2 K and atmospheric pressure

Chenguang Xie, Tao Zhang, Xinlong Wang, Benhe Zhong, Shengwei Tang*

Multi-phase Mass Transfer and Reaction Engineering Lab, School of Chemical Engineering, Sichuan University, Chengdu, 610065, China

ARTICLE INFO

Article history:
Received 2 May 2018
Received in revised form
5 July 2018
Accepted 16 July 2018
Available online 17 July 2018

Keywords:
Diammonium hydrogen phosphate
Ammonium dihydrogen phosphate
Urea
Potassium sulfate
Phase equilibrium
Liquid fertilizer

ABSTRACT

Application of liquid fertilizers can significantly improve the fertilizer utilization efficiency and labor efficiency. Phase equilibrium of various fertilizers in aqueous solution is the basis of manufacturing liquid fertilizers. The solid-liquid phase equilibria of ternary systems $NH_4H_2PO_4 + CO(NH_2)_2 + H_2O$, $(NH_4)_2HPO_4 + CO(NH_2)_2 + H_2O$, $K_2SO_4 + CO(NH_2)_2 + H_2O$, $K_2SO_4 + NH_4H_2PO_4 + H_2O$ and $K_2SO_4 + (NH_4)_2HPO_4 + H_2O$ at 303.2 K were investigated by isothermal solution saturation method. The maximum nutrient content of $(NH_4)_2HPO_4 + CO(NH_2)_2 + H_2O$ solution is 31.78 wt% at the saturated solution of $(NH_4)_2HPO_4$, and the mass ratio of N: P_2O_5 is 1: 2.53. In the solutions of $NH_4H_2PO_4 + CO(NH_2)_2 + H_2O$, $K_2SO_4 + CO(NH_2)_2 + H_2O$ and $K_2SO_4 + (NH_4)_2HPO_4 + H_2O$, the corresponding maximum of nutrient contents all are obtained at the corresponding invariant points as 33.82 wt%, 27.32 wt% and 32.92 wt% respectively. And the mass ratios of nutrients are N: P_2O_5 of 2.69: 1, K_2O: N of 1:15.66 and N: P_2O_5: K_2O of 1.64: 4.15: 1, respectively. The maximal nutrient content in the $K_2SO_4 + NH_4H_2PO_4 + H_2O$ saturation solution is 25.14 wt% and the corresponding mass ratio of N: P_2O_5: K_2O is 1.26: 6.38: 1. Based on the phase equilibrium diagrams, the species and nutrient contents in liquid fertilizers all are adjustable by choosing different raw materials or modulating the prescription. The results provide fundamental data for the preparation of liquid fertilizers. It is also helpful to optimize the operation parameters in the manufacturing process, storage process or application process to avoid the precipitation of solid.

1. Introduction

Fertilizers are the food of foodstuff. Nitrogen, phosphorus and potassium are three indispensable nutrients for plant growth [1]. Fertilizers make a tremendous contribution to solve the global problem of food shortage [2–4]. During the last fifty years, fertilizers consumption increased gradually [5]. Usually, a specific chemical fertilizer only contains one or two primary nutrients. For example, potassium dihydrogen phosphate contains two nutrients including potassium and phosphorus [6,7]. Conventional fertilizers are commonly applied and sold in a solid state. The traditional fertilizing method is difficult to realize scientific fertilization because only single or imbalance nutrients are fertilized. It leads to excess of specific nutrient or serious lack of other nutrients needed by plants. Although fertilizers are fed to the plant by a prescription, the proportions of nutrients absorbed by plants are difficult to meet the expectation for the loss of nutrients and the difference of adsorption efficiency between different nutrients. Even more, traditional fertilizing methods lead to low efficiency of nutrient uptake, serious nutrient loss and environmental problems, such as the eutrophication and pollution of surface and sea water [5,8–10]. Therefore, it is difficult to achieve the goal of scientific fertilization by traditional way.

Compared with conventional solid fertilizers, application of fluid fertilizers can improve the utilization efficiency of fertilizers and reduce the negative impacts on the environment [11]. Suspension fertilizer and liquid fertilizer are two major types of fluid fertilizers. For suspension fertilizers, nutrients or materials are partially dissolved in water and others are suspended in the solution uniformly. For liquid fertilizers, all the ingredients are dissolved in water completely. Fluid fertilizer can contain all the essential nutrients for plant growth, including phosphorus, nitrogen, potassium, calcium, magnesium and other micronutrients. The prescription is adjustable according to the demand of crops. Liquid fertilizer is easily transported to the root of plants and is absorbed

* Corresponding author.
E-mail addresses: 2015223075172@stu.scu.edu.cn (C. Xie), zhangtao@scu.edu.cn (T. Zhang), wangxl@scu.edu.cn (X. Wang), zhongbenhe@163.com (B. Zhong), tangdynasty@scu.edu.cn (S. Tang).

https://doi.org/10.1016/j.fluid.2018.07.016
0378-3812/

efficiently by plants. Fluid fertilizers are very easy to distribute in the field. Especially, the distribution of liquid fertilizers can be easily realized by spray irrigation and trickle irrigation. Although liquid fertilizers have many advantages, fundamental data are lacked to provide enough information for the preparation of liquid fertilizers with high content of nutrients and adjustable prescription. In the practices, crystallization or precipitation of compounds from the solution are usually occurred in the processes of storage or utilization, which lead to the blockage of the irrigation system and the system cannot work efficiently.

In order to provide necessary fundamental data for the preparation and application of liquid fertilizers, the solid-liquid phase equilibria of the aqueous solutions of ammonium dihydrogen phosphate (MAP, $NH_4H_2PO_4$), diammonium hydrogen phosphate (DAP, $(NH_4)_2HPO_4$), urea ($CO(NH_2)_2$) and potassium sulfate (K_2SO_4) are studied in this work. These four fertilizers contain one secondary element sulfur (S) and three primary elements, including nitrogen (N), phosphorus (P) and potassium (K). These nutrients all are necessary elements for the growth of plants [8]. They are commonly used as bulk fertilizers in agriculture [12,13]. And they are frequently used as raw materials for the manufacture of liquid fertilizers. The results provide essential information to the adjustment of liquid fertilizers prescriptions and the prevention of blocking in the processes of storage and utilization of liquid fertilizers. The aqueous solutions of the four fertilizers can form six ternary systems including $NH_4H_2PO_4 + CO(NH_2)_2 + H_2O$, $(NH_4)_2HPO_4 + CO(NH_2)_2 + H_2O$, $K_2SO_4 + CO(NH_2)_2 + H_2O$, $NH_4H_2PO_4 + (NH_4)_2HPO_4 + H_2O$, $K_2SO_4 + NH_4H_2PO_4 + H_2O$ and $K_2SO_4 + (NH_4)_2HPO_4 + H_2O$. Some fragmentary information about the equilibrium of these systems can be found from the literature. The phase equilibrium of $NH_4H_2PO_4 + CO(NH_2)_2 + H_2O$ at 263.2 K - 298.2 K and the invariant points of $(NH_4)_2HPO_4 + CO(NH_2)_2 + H_2O$ from 256.2 K to 323.2 K have been reported [14,15]. The phase equilibrium of $K_2SO_4 + CO(NH_2)_2 + H_2O$ at 298.2 K [16,17], and $NH_4H_2PO_4 + (NH_4)_2HPO_4 + H_2O$ at 303.2 K [18] are also found from literature. However, these results are not enough to provide plenitudinous information for the preparation of liquid fertilizers. In this work, the phase equilibria of $NH_4H_2PO_4 + CO(NH_2)_2 + H_2O$, $(NH_4)_2HPO_4 + CO(NH_2)_2 + H_2O$, $K_2SO_4 + CO(NH_2)_2 + H_2O$, $K_2SO_4 + NH_4H_2PO_4 + H_2O$ and $K_2SO_4 + (NH_4)_2HPO_4 + H_2O$ at 303.2 K and atmospheric pressure are studied systematically to provide essential information for the production and application of liquid fertilizers.

2. Experimental section

2.1. Materials and instruments

Ultrapure water (electric conductivity $\leq 1\ 10^{-4}$ S m^{-1}) was used in this study. Purity and sources of chemicals used in this study are listed in Table 1. All chemicals were used without further purification.

A thermostat water bath (CY50A, Shanghai Boxun Medical Biological Instrument Corporation, Shanghai, China) was employed for phase equilibrium study. The water bath temperature was controlled within ±0.01 K. An analytic balance (FA2004B, ShangHai Jingke Tianmei Instrument Co., Ltd, Shanghai, China) was used to weigh the mass of samples with uncertainty of ±0.0001 g. An X-ray diffraction (XRD) analyzer (DX2700, Dandong Haoyuan Instrument Co., Ltd, Liaoning, China) was used to characterize the sample of solid phase.

2.2. Experimental methods and procedures

The solid-liquid equilibrium of these ternary systems was determined by the method of isothermal solution saturation described elsewhere [6,24–26]. During equilibrium experiments, the solution was sampled and analyzed according to the methods described in Table 1. The results show that 15 h are enough to reach phase equilibrium.

Take the ternary system $NH_4H_2PO_4 + CO(NH_2)_2 + H_2O$ as an example, a certain amount of $NH_4H_2PO_4$, $CO(NH_2)_2$ and water were filled into a 250 ml three-neck round-bottom flask equipped with a mechanical stirrer. The flask was sealed and immersed into the water bath. The equilibrium temperature was controlled at 303.2 K. The accuracy of temperature was guaranteed by a mercury thermometer (precision of ±0.1 K). The mixtures were kept at the preset temperature over 24 h under stirring. Then the mixture was kept in the thermostatic water bath without stirring for at least 10 h to settle down solids. The saturation solution was sampled to analyze its compositions. The density of the saturation solution was measured by a 10 ml pycnometer with a relative standard uncertainty of 0.0002 [27,28]. Compositions of wet solid were measured by Schreinemaker's method [29]. The solid sample was characterized by XRD after drying over 3 h at 303.2 K.

2.3. Analytical methods

The mass fraction of phosphorus pentoxide (P_2O_5) was measured by a quinoline phosphomolybdate gravimetric method [19,20] with a relative standard uncertainty of 0.0036. The mass fraction of potassium oxide (K_2O) was determined by a sodium tetraphenylborate gravimetric method [17] with a relative uncertainty of 0.0027. The mass fraction of ammonium ion (NH_4^+) was determined by a method of distillation combined with acid-base titration [30] with a relative standard uncertainty of 0.0035. The mass fraction of urea was determined by a titration method after distillation process [21,22] with a relative standard uncertainty of 0.0038. The titration was done by a 50 ml burette with methyl red and methylene blue as indicators. The titration uncertainty was ±0.05 ml. The water content was calculated based on the material balance. The relative standard uncertainties of the measurement in the study were calculated with the EURACHEM/CATAC Guide [31].

The contents of P_2O_5 and K_2O in the liquid phase were obtained according to the analytical process. The content of N was calculated according to the mass fraction of the solutes in the liquid phase.

Table 1
Purity and sources of chemicals used in this study.

Chemical[a]	Abbreviation	Purity (Mass fraction)	Source	Analytical method
$NH_4H_2PO_4$	MAP	≥0.990	Chengdu Kelong Chemical Reagent Co. Ltd., China	Quinoline phosphomolybdate gravimetric method [19,20]
$(NH4)_2HPO_4$	DAP	≥0.990	Chengdu Kelong Chemical Reagent Co. Ltd., China	
$CO(NH_2)_2$	U	≥0.990	Chengdu Kelong Chemical Reagent Co. Ltd., China	Titration method after distillation process [21,22]
K_2SO_4	K	≥0.990	Chengdu Kelong Chemical Reagent Co. Ltd., China	Sodium tetraphenylborate gravimetric method [17,23]

[a] $NH_4H_2PO_4$, ammonium dihydrogen phosphate; $(NH_4)_2HPO_4$, diammonium hydrogen phosphate; $CO(NH_2)_2$, urea; K_2SO_4, potassium sulfate.