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Interaction Studies of Calcium Dihydrogen Phosphate with Sulphate Salt

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The interaction of calcium dihydrogen phosphate with copper, zinc and cobalt sulfate salts in dilute solutions (0.01 M) at 303.15 and 353.15 K, depending on the $Ca(H_2PO_4)_2$:MSO_4 ratio, was studied. It is found that at a molar ratio of 1:1, the pH, electrical conductivity, viscosity and density have extreme values, which indicates a change in the composition of solutions. The results of chemical analysis at a ratio of of 1:1 showed the formation of calcium sulfate and hydrogen phosphates of copper, zinc and cobalt, regardless of temperature. This indicates that calcium dihydrogen phosphate undergoes hydrolysis in an aqueous medium and then an exchange reaction occurs between microelement sulfates and calcium hydrogen phosphate. The addition of phosphoric acid into mixing solutions prevents the hydrolysis of calcium dihydrogen phosphate and the reaction products were calcium sulfate and dihydrophosphates of copper, zinc and cobalt.

Keywords: Calcium dihydrogen phosphate, Metals sulfate, Dihydrogen phosphates, Hydrogen phosphates.

INTRODUCTION

One of the most affordable concentrated single phosphate fertilizers, double (triple) superphosphate is appropriate for use on all crops and soil types [1-3]. The production of single superphosphate (SSP) involves a direct interaction between phosphate rock concentrates and sulfuric acid in the presence of water resulting in the complicated chemical reactions [4]. Extractive phosphoric acid derived from low-grade phosphorites is unsuitable for double superphosphate production due to its excessive impurity levels, particularly magnesium, which prevents concentration through vacuum evaporation to a P_2O_5 level above 38% and results in thickening issues [5-7]. The production of double superphosphate is obtained by the decomposition of phosphate containing raw materials with phosphoric acid. Initially, the breakdown of phosphorite molecules takes place, resulting in solutions which lack reaction products then in the second stage, a solution saturated with calcium phosphates resulting to the crystallization on the surface of phosphates and mainly consists of calcium dihydrogen phosphate monohydrate [8].

The main disadvantage of phosphorus containing fertilizers is their low efficiency in nutrient use. During the initial year of application, roughly 20-25% of phosphorus is utilized, followed by an estimated 40% usage during the subsequent 2-3 years [9,10]. The implementation of microelements into phosphate fertilizers is one approach to improve their utilization efficiency [11,12]. Research indicates that even insufficient single microelements in the soil prevents an increase in raw cotton output, even when high dosages of nitrogen-phosphorus fertilizers are used and other agricultural practices are followed too. To enhance the utilization of phosphate fertilizer and devise a method for producing the double superphosphate with trace elements, viscosity, density, specific electrical conductivity, and hydrogen ion concentrations were employed to assess the interaction between calcium dihydrogen phosphate and the sulfates of zinc, copper and cobalt in diluted solutions, based upon the ratio of dihydrophosphate to microelement sulfate [13].

While incorporating SSP into composts might enhance phosphorus availability and reduce nitrogen loss, there has been limited investigation into the impact of SSP on the transformation of carbon fractions throughout the composting process. This study sought to determine how various SSP constituents, such as calcium dihydrogen phosphate, calcium sulfate and free acid, affected the maturity and decomposition of organic matter during the composting of pig manure [14]. As universal adhesives, 10-methacryloyloxidecyl dihydrogen phosphate monomer (10-MDP) is frequently utilized as a bonding monomer. The chemical interaction of 10-MDP with hydroxyapatite in hard tissue to form calcium salts enables the adhesives containing this monomer to directly engage with the surrounding periodontium [15].

In this work, 0.01 M solutions of copper sulfate, zinc sulfate, cobalt sulfate and calcium dihydrogen phosphate were prepared. A mixture of components at various ratio was thermostated at 303.15 K and then studied their pH, electrical conductivity, viscosity and density. Then, impact of four types of compounds, for example, calcium carbonate, calcium silicate, potassium alginate and potassium dihydrogen phosphate, were evaluated for their pasting behaviour, rheological properties, microstructure, water mobility and textural characteristics of pastes, dough and high-moisture starch hydrogels derived from potato starch [16].

EXPERIMENTAL

All the compounds used in this work were of analytical grade. For chemical investigation and measurements of a series of laboratory prepared solutions, double deionized water with a conductivity below 1×10^{-4} S m^{-1} at room temperature was used. The chloride content was determined using the mercuric nitrate titration method, with an error in mass fraction of 0.003. Using sodium tetraphenylborate precipitation method, the K$^+$ concentration was determined with a mass fraction ± 0.0005, whereas the B_5O_8 concentration was calculated using a gravimetric technique using mannitol and NaOH reference solution.

RESULTS AND DISCUSSION

In $nMSO_4$-$Ca(H_2PO_4)_2$ (M = Cu, Co or Zn) systems and n is the ratio of monocalcium phosphate to microelement sulfate, the results of the salt interactions in the aqueous phase are shown in Figs. 1-3. These systems were studied from n = 0.25 to n = 3.5. The variations in viscosity and density based on the proportion of monocalcium phosphate to trace element sulfates reach significant fluctuations at n = 1, which confirmed the modification in the composition of the solution. In order to determine the salt content of the byproducts of the interaction between these compounds, metal sulfate solutions of microelements and monocalcium phosphate were prepared at a ratio of 1:1 based on the results obtained. Following the aqueous and solid phases' separation, the precipitate was first washed with acetone followed by double distilled water while determining the content of various components in the solid phase.

As the ratio of monocalcium phosphate to microelement sulfate increases, the specific electrical conductivity of the solutions progressively increases, while the pH of the solutions gradually decreases as both curves exhibit distinctive inflections at n = 1.

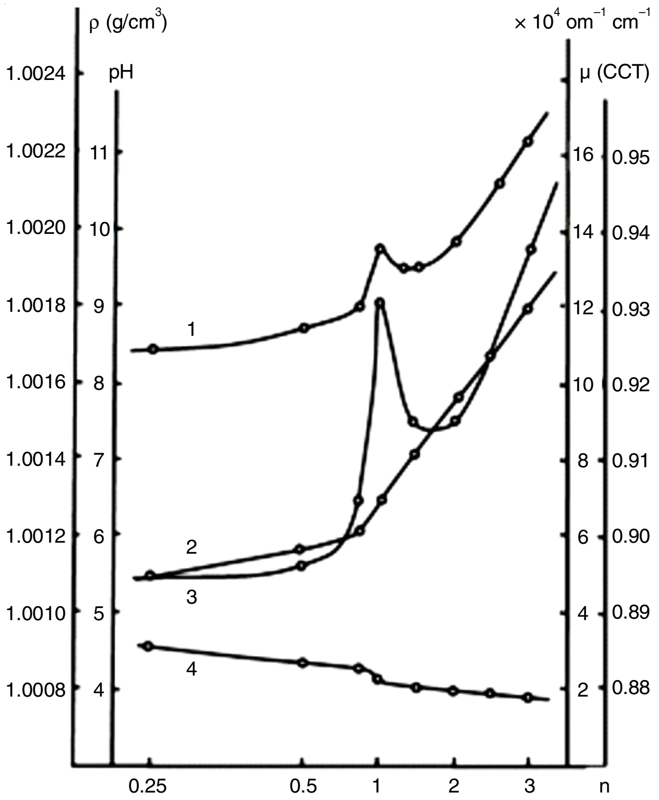

Fig. 1. Changes in viscosity (1), density (2), specific electrical conductivity (3) and pH (4) of solutions depending on the ratio of monocalcium phosphate to copper sulfate

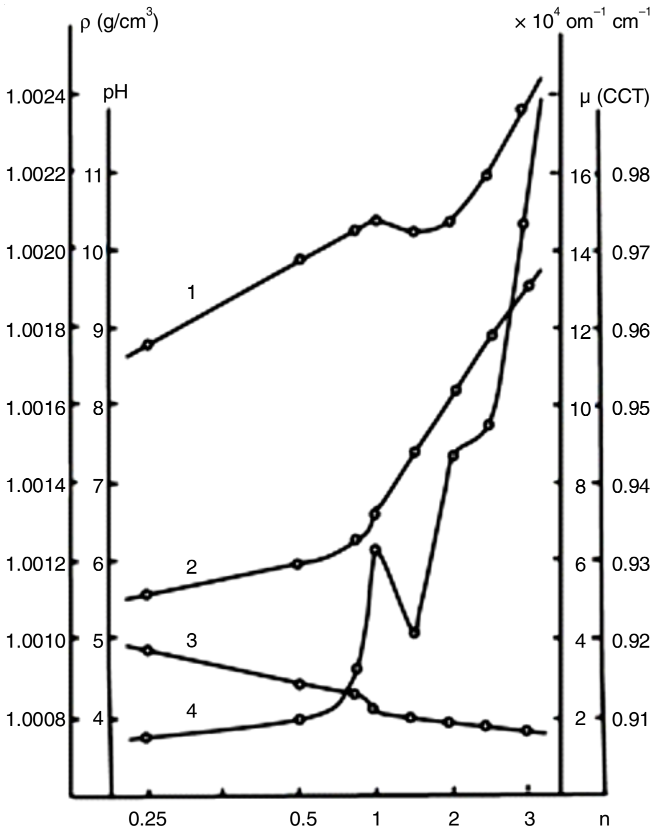

Fig. 2. Changes in viscosity (1), density (2), specific electrical conductivity (3) and pH (4) of solutions depending on the ratio of monocalcium phosphate to zinc sulfate

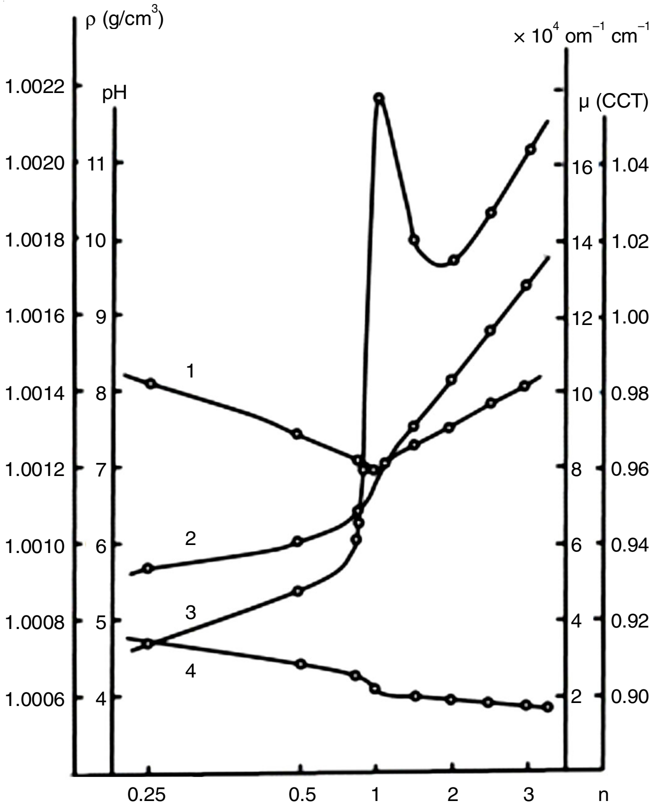

Fig. 3. Change in viscosity (1), density (2), specific electrical conductivity (3) and pH (4) of solutions depending on the ratio of monocalcium phosphate to cobalt sulfate

The products of the reaction between zinc sulfate, copper sulfate, cobalt sulfate and monocalcium phosphate at 30 ºC are analyzed and found that interaction products are calcium sulfate and disubstituted phosphates of microelements (Table-1). The absence of trace elements and sulfate ions in the washing acetone solution, which are readily soluble in acetone indicates the interaction of these salts with monocalcium phosphate with conversion to phosphates.

As the aqueous extract obtained after acetone washing, no phosphate ions were detected. This indicates the absence of monosubstituted phosphates in the solid phase. Thus, it can be assumed that when zinc sulfate, copper sulfate, cobalt sulfate interact with the monocalcium phosphate in an aqueous medium, the phosphate undergoes hydrolysis followed by an exchange reaction between the metal sulfate and the disubstituted calcium phosphate.

$$Ca(H_2PO_4)H_2O + H_2O \longrightarrow CaHPO_4{\cdot}2H_2O + H_3PO_4$$

$$CaHPO_4{\cdot}2H_2O + MSO_4{\cdot}NH_2O \longrightarrow$$
$$MHPO_4{\cdot}2H_2O + CaSO_4{\cdot}2H_2O + (n\text{-}2)H_2O$$

To confirm this reaction pathway, the interactions between trace element sulfates and monocalcium phosphate in 15% phosphoric acid solution. In this instance, we performed based on the subsequent considerations: Firstly, phosphoric acid is the primary constituent in the synthesis of double superphosphate and secondly, the hydrolysis of monocalcium phosphate can be mitigated by injecting phosphoric acid, so shifted reaction 2.24 to the left.

After washing the isolated solid phase first with acetone and then with water, trace elements and phosphate ions pass into the aqueous extract. The compositions of the aqueous and solid phases reveal the presence of calcium sulfate and trace element monosubstituted phosphates, both of which exhibit high solubility in water. At 353.15 K, the interaction of monocalcium phosphate with trace element sulfate salts revealed the presence of calcium sulfate and disubstituted phosphates of Cu, Zn and Co in the solid phase. The reaction of these components in the presence of a 15% phosphoric acid solution results in the formation of water-insoluble calcium and trace element compounds, such as disubstituted phosphates of Cu, Zn and Co.

Conclusion

In this work, the interactions between zinc sulfate, copper sulfate, cobalt sulfate and monocalcium phosphate were established. The interaction of microelement sulfate with monocalcium phosphate due to the hydrolysis, results in the formation of calcium sulfate and disubstituted microelement phosphates as products. The incorporation of phosphoric acid has demonstrated the effectiveness in inhibiting the hydrolysis process. The reaction products in this case consist of calcium sulfate and water-soluble monosubstituted phosphates of Cu, Zn and Co.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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TABLE-1
THE SALT AND CHEMICAL COMPOSITION OF THE PRODUCTS OF THE INTERACTION OF TRACE ELEMENT SULFATE SALTS WITH MONOCALCIUM PHOSPHATE AT 303.15 K

Reactions	Trace element	P_2O_5	CaO	SO_4	Composition
Solid phase composition					
$CuSO_4 + Ca(H_2PO_4)_2 + H_2O$	8.04	9.45	26.67	43.26	$CuHPO_4 + CaSO_4$
$ZnSO_4 + Ca(H_2PO_4)_2 + H_2O$	5.38	5.97	27.72	47.33	$ZnHPO_4 + CaSO_4$
$CoSO_4 + Ca(H_2PO_4)_2 + H_2O$	3.95	4.61	30.03	50.81	$CoHPO_4 + CaSO_4$
Composition of the solid phase's aqueous extract following the addition of phosphoric acid					
$CuSO_4 + Ca(H_2PO_4)_2 + 15\%H_3PO_4$	0.63	1.38	0.19	0.33	$Cu(H_2PO_4)_2 + CaSO_4$
$ZnSO_4 + Ca(H_2PO_4)_2 + 15\%H_3PO_4$	0.73	1.60	0.17	0.34	$Zn(H_2PO_4)_2 + CaSO_4$
$CoSO_4 + Ca(H_2PO_4)_2 + 15\%H_3PO_4$	0.54	1.32	0.17	0.35	$Co(H_2PO_4)_2 + CaSO_4$

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