

Raman and Infrared Spectroscopic Studies of Divalent Cation Phosphate Hydrates Related to Saline Soil

การศึกษาฟอสเฟตไฮเดรตของแคตไอออน (II) ที่สัมพันธ์กับดินเค็ม โดยวิธีสเปกโทรสโกปีรามานและอินฟราเรด

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ABSTRACT

The intermolecular interaction in divalent cation phosphate hydrates related to saline soil were studied for $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (bobierrite) and $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (newberyite) that isostructure with $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (vivianite) and $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$, by Raman and Infrared Spectroscopy and isotopic dilution technique. The observed OH stretching of water in phosphate hydrates and uncoupled ν_{OH} (HOD) vibration in D_2O condition lead to the estimation of the intermolecular distance between oxygen water and anion oxygen ($R_{\text{O...O}}$) and enthalpy of hydrogen bonding ($-\Delta H_{\text{H}}$) by using equation $R_{\text{O...O}} = 3.764 - 0.169 \ln \Delta \nu_{\text{OH}}(\text{HOD})/\text{cm}^{-1} \text{ \AA}$ and $-\Delta H_{\text{H}} = 1.286 + 0.0418 \Delta \nu_{\text{OH}}(\text{HOD})/\text{cm}^{-1} \text{ kJ/mol}$, respectively. The $R_{\text{O...O}}$ and $-\Delta H_{\text{H}}$ for $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, and $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$ were found to be 2.730, 2.707, 2.790, and 2.799 $\text{\AA}$ and -20.231, -23.297, -14.547, and -13.892 kJ/mol OH, respectively. The mole number of water of crystallization of octahydrate and trihydrate were studied by thermochemical and Karl-Fischer methods, and found to be 8 and 3 moles, respectively. The phosphate hydrates prepared from the variation of cation mole ratios; Fe(II)/Mg(II) and Mn(II)/Mg(II) in 5 categories, 1:1, 1:2, 1:3, 2:1 and 3:1 were studied. The data from FT-IR showed the spectrum characterized for $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$, $(\text{Mg}, \text{Fe})_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, $(\text{Mg}, \text{Mn})\text{HPO}_4 \cdot 3\text{H}_2\text{O}$. Moreover, the effects of ionic strength approximating salinity levels on the precipitation of compounds were investigated. Initial pH of the phosphate hydrates preparations were followed up for four salinity levels. It was found that the initial pH for those 4 phosphate hydrates is as follow: $S_{\text{ns}} < S_{\text{ss}} \approx S_{\text{ms}} \approx S_{\text{vs}}$.

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บทคัดย่อ

ได้ศึกษาอันตรกิริยาระหว่างโมเลกุลในฟอสเฟตไฮเดรตของแคตไอออน (II) ที่สัมพันธ์กับดินเค็ม โดยไฮเดรตที่ศึกษา คือ $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (โบเบียร์ไรท์) และ $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (นิวเบอไรท์) ซึ่งมีโครงสร้างเหมือนกันกับ $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (วิเวียไนท์) และ $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$ ตามลำดับ ด้วยวิธีสเปกโทรสโกปีรามาน และอินฟราเรดและเทคนิคการเจือจางด้วยไอโซโทป ค่าความถี่การสั่นแบบยืดหดพันธะของหมู่ OH ของน้ำในฟอสเฟตไฮเดรตและการสั่นแบบไม่คู่ควบของหมู่ $\text{OH}(\nu_{\text{OH}} \text{HOD})$ ที่อยู่ในสภาพแวดล้อม D_2O สามารถนำไปประมาณค่าระยะ $R_{\text{O...O}}$ ตามสมการ $R_{\text{O...O}} = 3.764 - 0.169 \ln \Delta \nu_{\text{OH}}(\text{HOD})/\text{cm}^{-1} \text{ \AA}$ และค่าเอนทาลปีของพันธะไฮโดรเจน ($-\Delta H_{\text{H}}$) ตามสมการ $-\Delta H_{\text{H}} = 1.286 + 0.0418 \Delta \nu_{\text{OH}}(\text{HOD})/\text{cm}^{-1} \text{ kJ/mol}$ พบว่าค่าระยะ $R_{\text{O...O}}$ และ $-\Delta H_{\text{H}}$ สำหรับ $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ และ $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$ เท่ากับ 2.730, 2.707, 2.790 และ 2.799 $\text{\AA}$ และ -20.231, -23.297, -14.547, และ -13.892 kJ/mol OH ตามลำดับ จำนวนโมลน้ำในผลึกออกตะไฮเดรตและไตรไฮเดรตศึกษาโดยอาศัยสมบัติทางความร้อนและวิธีคาร์ล - ฟิชเชอร์ พบว่ามีจำนวนโมลน้ำในผลึกมีค่าเป็น 8 และ 3 ตามลำดับ ลักษณะการเกิดฟอสเฟตไฮเดรตจากแคตไอออนผสมตามการเปลี่ยนแปลงสัดส่วนจำนวนโมล Fe(II)/Mg(II) และ Mn(II)/Mg(II) ใน 5 สัดส่วนคือ 1:1, 1:2, 1:3, 2:1 และ 3:1 จากข้อมูล FT-IR แสดงสเปกตรัมเอกลักษณ์สำหรับ $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$, $(\text{Mg}, \text{Fe})_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, และ $(\text{Mg}, \text{Mn})\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ นอกจากนั้นยังได้ศึกษาอิทธิพลของความแรงไอออนที่เป็นตัวกำหนดระดับความเค็มที่มีผลต่อการตกตะกอนของฟอสเฟตไฮเดรต จากนั้นติดตามการเปลี่ยนแปลง pH เริ่มต้นของการเตรียมฟอสเฟตไฮเดรตทั้ง 4 ชนิด แสดงการเปลี่ยนแปลงค่า pH ดังนี้: $S_{\text{ns}} < S_{\text{ss}} \approx S_{\text{ms}} \approx S_{\text{vs}}$

คำสำคัญ : โบเบียร์ไรท์ นิวเบอไรท์ วิเวียไนท์

Key Words : Bobierite, Newberyite, Vivianite

Introduction:

The intermolecular interaction between water and ions or other molecules principally determine the structure and properties of the corresponding solid and liquid states. Solid hydrates are suitable for studying hydrogen bonding for their specific geometries. Hydrogen bonding is one of the most important interactions, playing an important role in many chemical processes. Vibrational spectroscopy (IR and Raman) are known to be the most powerful method for investigating hydrogen bonding and the structure of aqueous systems. Changes in the vibrational band provide the information about the structure of the associated

water molecules. The scope of this work will focus on the hydrogen bonding for ion-water interactions in phosphate hydrates of divalent cations namely magnesium, iron and manganese. The related local problem of salt affected soil in Northeast Thailand is the precipitation of iron and manganese phosphates. Some magnesium phosphate hydrates have the isostructural property related to selected hydrates Mn(II) and Fe(II), therefore Mg(II) phosphate hydrates are included in the study. Dryland salinization causes great impact to the economy and environmental problem in Northeast Thailand. The experimental conditions were carried out to represent the soil salinity levels.

Methodology:

The $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ was prepared by mixing 1.5 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 1 M H_3PO_4 with the cation:anion mole ratio of 3:2. The solution was cooled in the ice bath and then added dropwise of 3 M NaOH with continuous stirring until the pH was 9. The obtained gel was allowed to stand for 24 h, filtered, and suspended in distilled water. After that 30 min of stirring was needed and allowed to stand for 24 h, filtered, and air-dried. The precipitates of $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ were prepared by adding 0.1 M $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ to a constantly stirred solution of 0.067 M K_2HPO_4 and neutralized to pH = 6.5 by using concentrated ammonium hydroxide. The precipitates were kept in contact with the mother liquor for 7 days without stirring. The solution pH was monitored daily and adjusted to pH = 6.5. After 7 days, the precipitates were filtered by suction pump and washed several times with deionized water. The precipitates were kept in the dessicator. The $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ was obtained by dropwise addition of equivalent moles of 0.5 M H_3PO_4 over an aqueous suspension of 0.5 M $\text{Mg}(\text{OH})_2$ tempered in an ice bath under continuous stirring about 1 h after the complete addition. The resulting suspension was vacuum-dried. The crystals of $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$ were obtained by mixing 0.5 M $\text{MnCO}_3 \cdot x\text{H}_2\text{O}$ with 0.5 M H_3PO_4 in the cation:anion mole ratio of 1:1. The solid was transferred to vial bottle and sealed with parafilm and kept in a dessicator. The deuterated analogues were prepared by using the D_3PO_4 instead of H_3PO_4 and K_2HPO_4 by the same method. The mole number of water of crystallization of the synthesized hydrates were determined by thermal analysis (TG/DTA, Perkin Elmer, Pyris Diamond),

gravimetric and Karl-Fischer method (Metrohm 798 MPT Titrino). The metal content in the synthesized hydrates were determined by atomic absorption spectrophotometry, (AAS, Perkin Elmer, Analyst 100). The precipitation of mixed two cations with isostructural properties $\text{Mg}(\text{II})/\text{Fe}(\text{II})$ and $\text{Mg}(\text{II})/\text{Mn}(\text{II})$ in 5 cation ratios namely 1:1, 1:2, 1:3, 2:1 and 3:1 were prepared. In order to simulate the experimental conditions close to the natural saline soil, sodium chloride were added to the reaction mixtures in various amounts corresponding to the salinity levels : non saline (S_{ns}), slightly saline (S_{ss}), moderately saline (S_{ms}) and very strongly saline (S_{vs}). The initial pH was monitored by pH measurement (SUNTEX pH/mV/TEMP. METER). The mid-IR vibrational spectra were recorded on an FTIR-FT Raman Spectrophotometer using KBr pellet and nujol mull technique. The vibrational bands were assigned and the uncoupled ν_{OH} HOD leads to the estimation of enthalpy of hydrogen bonding ($-\Delta H_{\text{H}}$), and $R_{\text{O...O}}$ distance.

Results and Discussion:

The results from FTIR spectra of $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$, and $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ showed the characteristic peaks of vibrational and librational modes of H_2O , PO_4^{3-} and HPO_4^{2-} . The $R_{\text{O...O}}$ and $-\Delta H_{\text{H}}$ for $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, and $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$ were found to be 2.730, 2.707, 2.790, and 2.799 Å and -20.231, -23.297, -14.547, and -13.892 kJ/mol OH, respectively. The results of TG/DTA, gravimetric and Karl-Fischer methods are in good agreement with 3 moles of water in $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$,

$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ whereas the water contents of $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ were found to be 8 moles for both TG/DTA with heating temperature range 30–800 °C and Karl–Fischer method. However 8 moles was found for $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ by Karl–Fischer method, which 7 moles by TG/DTA with the temperature program of 30–1000 °C. The complete elimination of water of this hydrate operated at higher temperature than 1000 °C. Atomic absorption spectroscopic technique provided the good agreements with 1 atom of metal per hydrate formula in $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, meanwhile $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ and $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ 3 atoms per hydrate formula were obtained. The mixed phosphate hydrates data from FT–IR showed the spectrum characterized for $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (Fe condition), $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$ (Mn condition), $(\text{Mg}, \text{Fe})_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (Mg condition), $(\text{Mg}, \text{Mn})\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ (Mg condition). Initial pH of the phosphate hydrates showed the changing of pH in such away that $S_{\text{ns}} < S_{\text{ss}} \approx S_{\text{ms}} \approx S_{\text{vs}}$.

Conclusion:

The vibrational spectroscopic studies are very powerful method for determination of solid hydrates in terms of sample characterization, structural and bonding features.

This study, the intermolecular interactions in $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$, and $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ are studied by using FTIR/ FT Raman spectroscopy. The frequency shift of ν_{OH} (HOD) leads to the estimated enthalpy of hydrogen bonding ($-\Delta H_{\text{H}}$) and $R_{\text{O...O}}$ distances.

The thermal properties of all hydrates were studied by using TGA/DTG/ DTA and DSC techniques. The mole numbers of crystallization water of these hydrates were characterized by using TGA/DTG/DTA and Karl – Fischer methods. The metal stoichiometry was determined by using atomic absorption spectroscopy (AAS). The mole numbers of crystallization water and metal content were used to confirm the empirical formula of each hydrate.

The effect of ionic strength on the precipitations of $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$, and $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ and the mixed cation mole ratios; Fe(II)/Mg(II) and Mn(II)/Mg(II) were studied to predict the precipitation of iron and manganese phosphate hydrates that related to the ferrollysis process in Northeast, Thailand saline soils.

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