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Investigation of water structure changes in solutions: H_2O-$CO(NH_2)_2$ – phosphate [K_3PO_4, K_2HPO_4, KH_2PO_4] using ultraacoustic method

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Introduction

Properties of carbamide and its significance in every day life are described in literature [1]. Phosphates are used widely in agriculture as mineral fertilisers. Phosphorus is an indispensable macroelement in all organisms. It can be found in vegetables, leguminous plants, bones, dentine, brain cells, muscles, animal and human organs. Phosphorus combinations can be found in brain, nerves and blood structures. Phosphorus combinations, especially macroergical ones, concentrate and deposit energy that is used for physiological functions in a human body. Phosphorus salts maintain proper acidity, osmosis pressure, biocolloidical physical and chemical properties. Deficiency of phosphorus causes necrosis and other physiological disorders in plants, and ostheophorosis and other bone diseases for human beings and animals. Lack of phosphorus slows down growth; weakness, progressive losing of flesh and death appear. Adult needs 1,0-1,2 grams of phosphorus in twenty four hours.

Potassium is chemically a very active element. Potassium is one of biogenical elements and it can be found in all plants and animals. Plants take potassium from soil. When plants are short of potassium, their growth is of little value, and they more often are ill. Animals receive potassium with food. Many sea organisms take potassium from water. Adult needs 2-3 grams of potassium in twenty four hours. In organisms potassium concentrates mostly in cells. Potassium ions help to regulate generation of biocolloidical potentials and spreading of neural impulses, systole and muscle contraction, maintain osmosis pressure, help cell colloids to connect water, activate some ferments, participate in albumen biosynthesis, carbohydrate metabolism, photosynthesis and respiration.

Phosphates are salts of phosphorus acid. Salts of orthophosphorus acid are called orthophosphates. There are three kinds of orthophosphates: primary or dihydrophosphates (KH_2PO_4), secondary or hydrophosphates (K_2HPO_4) and tertiary or normal phosphates (K_3PO_4). Potassium orthophosphates dissolve in water and that is why they are used as phosphorus fertilisers. In water potassium orthophosphates decompose into ions. It is not quite clear what ions of potassium orthophosphates form in water. In this work we try to demonstrate what ions of potassium orthophosphates can be formed in water. We also investigated influence of phosphates on water structure dissolving potassium orthophosphates in a solution water – carbamide. If we dissolve substance in water, and in such a solution molecules of the substance are uncompressible, adiabatic compression lessens and quagmire increases.

Average uncompressible volume of one molecule is calculated from the formula:

$$v = \frac{\Delta\beta}{\beta_0 n}, \tag{1}$$

where $\Delta\beta = \beta_0 - \beta; \beta_0, \beta$ are the coefficients of the adiabatic compressibility of water and solution, n is the number of molecules of dissolved substance in a unit of solution's volume (i.e. concentration of molecules of dissolved substance).

While dissolving in water two substances together, the average uncompressible volume for one molecule is equal to [1]:

$$v^1 = \frac{\Delta\beta^1}{\beta_0 (n_1 + n_2)}, \tag{2}$$

where: $\Delta\beta^1 = \beta_0 - \beta'; \beta_0, \beta^1$ are the coefficients of the adiabatic compressibility of water and solution, where two substances are dissolved together, n_1 and n_2 are the quantities of the molecules of the both substances in a unit of volume of solution.

The aim of our work is to analyze how carbamide and phosphate dissolved together and separately influence a water structure.

Change of a water structure is estimated in accordance with difference of one molecule average uncompressive volume, dissolving substances together and separately, and calculated according to the formula:

$$\Delta v = \frac{\Delta\beta}{\beta_0 (n_1 + n_2)} - \frac{1}{2}\left(\frac{\Delta\beta_1}{\beta_0 n_1} + \frac{\Delta\beta_2}{\beta_0 n_2} \right). \tag{3}$$

There $\Delta\beta = \beta_0 - \beta, \beta_0$ is the coefficient of the water adiabatic compression, β is the coefficient of the carbamide and phosphate water solution, $\Delta\beta_1 = \beta_0 - \beta_1, \Delta\beta_2 = \beta_0 - \beta_2, \beta_1$ and β_2 are the coefficients of adiabatic compressibility of carbamide and phosphate, while dissolving them separately, n_1 and n_2 are the concentrations of carbamide and phosphate molecules.

Our investigations [1-4] show that uncompressible volumes of one salt molecule dissolved in water and found out using various methods, are larger than their crystallographic volumes (the sum of volumes of cations and anions).

Uncompressible volume of one molecule of dissolved salt consists of the sum of cation and anion volumes that are found from their crystallographic rays. The uncompressible layer of a polarized water molecule is formed about a cation because of strong electrostatic interaction with polar water molecules. Definition of a radius of the polarized water molecules layer is given in [4]. Theory of polarized water molecules layer about a cation was developed by P. Debay [6]. Water molecules in a polarized layer are deformed [4]. Two kinds of deformation in water molecules exist. Deformation depends on a cation's radius. Because of deformation of water molecules two kinds of the dispersive Van der Waals force are formed. The forces stipulate formation of water structure of two kinds. Change of a water structure is called hydration. If hydrogen connections among water molecules are strengthened by ions in electrolyte, we have positive hydration, if hydrogen water connections are weakened, we have negative hydration. The positive hydration lessens compressibility of a solution, and enlarges quagmire. The negative hydration influences on the contrary way. An anion does not form the uncompressible layer of polarized water molecules. An anion influences hydrogen connections of water molecules directly, and provokes positive or negative hydration in a solution. The ion NO_3^- does not influence hydrogen connections of water molecules [7,8,9], does not destroy the structure of water molecules. The Silver cation Ag^+ does not provoke hydration of a solution [10], it has a polarized layer of water molecules only. Therefore, the ions Ag^+ and NO_3^- are fundamental ions, and we can evaluate hydration influence of other ions in accordance with them. One valence cations, that have a crystallographic radius larger than 1,13 Å (are larger than crystallographic radius of Ag^+ cation), for example K^+, Rb^+, Cs^+, have a large crystallographic volume. They have a large layer of polarized water molecules [4], and their negative hydration influence on the growth of the adiabatic compressibility is not large. Small change of the adiabatic compressibility appears according to hydration of anions. Therefore, while dissolving potassium salts in water, they lessen adiabatic compressibility because of the uncompressible polarized layer of water molecules around a cation. The uncompressible volume of cation and anion and the size of the polarized layer of cation water molecules, while dissolving salts together and separately at the same temperature, have to be constant [6]. Therefore the change of one salt molecule average adiabatic volume, dissolving salts together and separately, depends only on the ions in a hydration solution.

Generalizing the results of investigation presented in [1-5], we can conclude, that according to the theory of compressibility, ions of all salts can be divided into two groups: hard and soft ions. The hard ions – cations – are the ions that have a strong polarized layer of water molecules: Na^+, K^+, Rb^+, Ag^+, Cs^+, Mg^{2+}, Ca^{2+}, Zn^{2+}, Sr^{2+}, Cd^{2+}, Ba^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Cu^{2+}, Al^{3+}, Ga^{3+}, Y^{3+}, In^{3+}, La^{3+}, Cr^{3+}, Fe^{3+}, Ce^3 - they are cations of all metals. The soft ions – anions are: F^-, Cl^-, Br^-, J^-, NO_3^-, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$. The cations NH_4^+, H^+, Be^{2+}, Li^+, that have no polarized layer of water molecules or it is very weak, can be attributed to the soft ions.

We have use the solvent water – carbamide $CO(NH_2)_2$ in our investigation. Carbamide is an organic substance. We make a precondition that carbamide does not dissociate into ions, and salts (potassium orthophosphates) that dissolve in water split into ions.

Methods of research

Change of a water structure due to dissolved salts in water, is evaluated from acoustic measurements. Ultrasound speed c was measured by the ultrasonic interferometer, the frequency of which is 10 MHz; uncertainty of measurements ± 0,02%. The density of solutions was measured by densimetrical method using a pycnometer, the volume of which is 50 cm^3, uncertainty of measurements is ± 0,001%. The coefficient β of the adiabatic compressibility can be found from the formula of ultrasound speed and density values:

$$\beta = \frac{1}{\rho c^2} \tag{4}$$

Error of calculation of adiabatic compressibility is ± 0,08%.

Bidistillator was used for investigation, and salts were chemically clean. Temperature was kept to within 0,05^{0}C. Measurements were carried out at the temperature of 25^{0}C. The results of measurements are represented graphically.

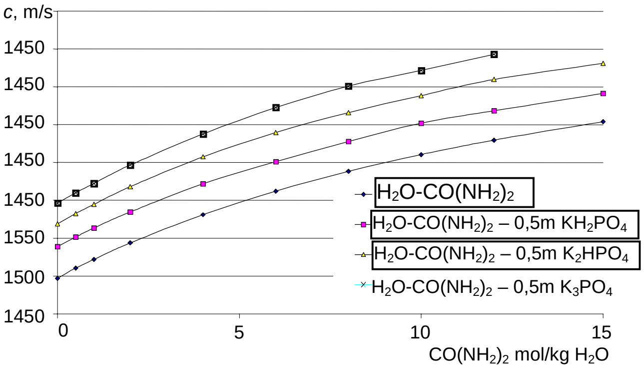

Fig.1. **Dependence of ultrasound speed *c* on concentration of carbamide in solutions**

Ultrasound velocity c versus concentration of carbamide in solutions is depicted in Fig.1. We can see that when the concentration of carbamide increases, the ultrasound speed c increases too. Phosphates increase the ultrasound speed in solutions, and potassium phosphate has the largest influence on the process.

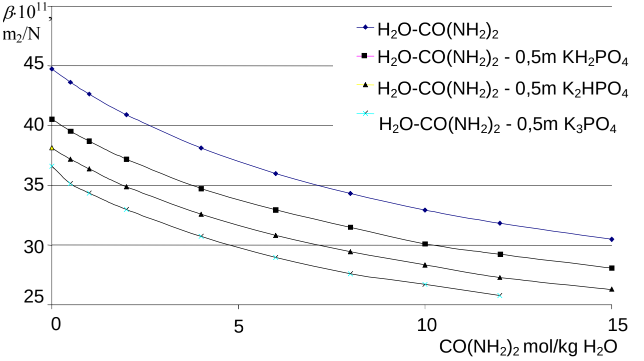

Fig.2. **Dependence of the coefficient of adiabatic compressibility β in solutions on concentration of carbamide**

Dependence of the coefficient of adiabatic compressibility β in solutions on concentration of carbamide is depicted in Fig. 2. We can see that when the concentration of carbamide increases, the adiabatic compressibility lessens. Phosphates reduce the adiabatic compressibility, and potassium phosphate has the largest influence. Decrease of the adiabatic compressibility can be explained by the existence of the large uncompressible polarized layer of potassium ion water molecules.

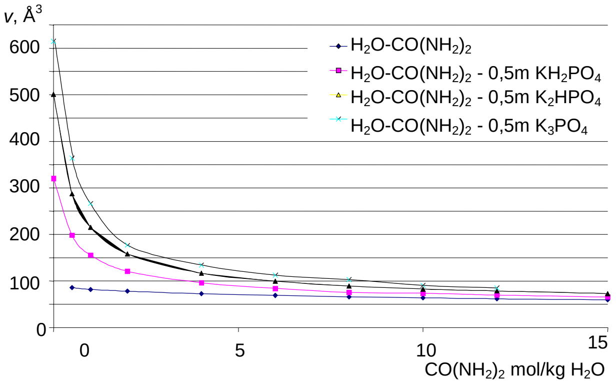

Fig.3. **Dependence of average uncompressible volume of one molecule of the dissolved substance on the concentration of carbamide, when carbamide and phosphate are dissolved together**

Dependence of the average uncompressible volume of one molecule of dissolved substance on the concentration of carbamide, when carbamide and phosphate are dissolved together, is depicted in Fig. 3. We can see that when the carbamide concentration increases, volume v suddenly lessens at the beginning and when carbamide concentration exceeds 5 mol/kg H_2O, volume v practically does not depend on the carbamide concentration. When carbamide concentration increases, the uncompressible polarized layer of water molecules suddenly lessens.

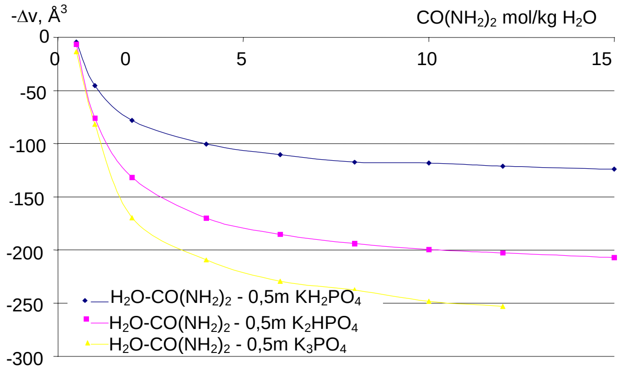

Fig.4. **Dependence of difference of average uncompressible volume of one molecule of dissolved substance Δv on carbamide concentration, when carbamide and phosphate are dissolved together and separately**

Dependence of difference of an average uncompressible volume of one molecule of dissolved substance Δv on carbamide concentration, when carbamide and phosphate are dissolved together and separately is depicted in Fig. 4. We can see that Δv has a negative value. Different concentration of free water molecules and different level of hydration can explain it, when both substances are dissolved together and separately. When the carbamide concentration increases and it is large (above 8 mol/kg H_2O), Δv absolute size almost does not depend on the concentration. Dependence of Δv on carbamide concentration can be explained by changes of and phosphate hydration.

Investigation of splitting of potassium orthophosphate molecules into ions

We shall try to calculate splitting of potassium orthophosphates by acoustic methods. The ion NO_3^- does not influence hydrogen connections [7,8,9] and the compressibility of a solution reduces due to its own uncompressible volume. The volume of the NO_3^- ion is 24,8 Å^3 [11]. The uncompressible volume of potassium nitrate that is obtained from acoustic measurements, is equal to 162,35 Å^3 [1]. The uncompressible volume of potassium ion gets 137,55 Å^3 (162,35 – 24,8 = 137,55). The salt K_3PO_4 splits in water according to the scheme:

$$K_3PO_4 \rightleftarrows 3K^+ + PO_4^{3-}.$$

The average uncompressible volume of K_3PO_4 is taken from acoustic measurements and is equal to 614,42 Å^3, and the uncompressible volume of the K^+ ion is 137,55 Å^3. PO_4^{3-} ion has the uncompressible volume of 202,07 Å^3 (614,72 – 3 · 137,55 = 202,07).

Two schemes of splitting are possible for the phosphate K_2HPO_4:

$$K_2HPO_4 \rightleftarrows 2K^+ + H^+ + PO_4^{3-}.$$

The average uncompressible volume of K_2HPO_4 molecule is equal to 500,6 Å^3 in water (Fig.3), and K^+ - 137,55 Å^3, PO_4^{3-} - 202,07 Å^3; hydrogen ion falls to 23,43 Å^3 (500,6 – 2 · 137,55 – 202,07 = 23,43).

The other splitting scheme of K_2HPO_4 is given by:

$$K_2HPO_4 \rightleftarrows 2K^+ + HPO_4^{2-}.$$

As the uncompressible volume of K_2HPO_4 is equal to 500,6 Å^3, and K^+ - 137,55 Å^3. The uncompressible volume of HPO_4^{2-} is equal to 225,5 Å^3. (500,6 – 137,55 =225,5).

Let potassium hydrophosphate splits in water according to three schemes. The first one:

$$KH_2PO_4 \rightleftarrows K^+ + 2H^+ + PO_4^{3-}.$$

It can be seen from Fig. 3, that the average uncompressible volume of one KH_2PO_4 molecule is equal to: 320,36 Å^3, and ions K^+ - 137,55 Å^3, H^+ - 23,43 Å^3, PO_4^- - 202,07 Å^3. The sum of uncompressible volumes of ions 66,12 Å^3 is larger than the uncompressible volume of one KH_2 PO_4 molecule (137,55 + 2 . 23,43 + 202,07 – 320,36 = 66,12). We think that this splitting is impossible. The second splitting scheme of the KH_2PO_4 salt in water can be like that:

$$KH_2PO_4 \rightleftarrows K^+ + H^+ + HPO_4^{2-}.$$

After putting the values of the uncompressible volume of ions, we get (137,55 + 23,43 + 225,5 =386,48). We can see that the sum of the uncompressible volumes of ions is larger than the uncompressible volume of KH_2PO_4 in 66,12

Å^3 (386,48 - 320,36 = 66,12). In our opinion, such a splitting is impossible too.

The third possible splitting scheme is the following:

$$KH_2PO_4 \rightleftarrows K^+ + H_2PO_4^-.$$

The uncompressible volume for the ion $H_2PO_4^-$ is 182,81 Å^3 (320,36 – 137,55 = 182,81). Summarizing results of calculations we can affirm that splitting of orthophosphates molecules into ions in water can be as follows:

$$K_3PO_4 \rightleftarrows 3K^+ + PO_4^{3-}$$

$$K_2HPO_4 \rightleftarrows 2K^+ + H^+ + PO_4^{3-} \rightleftarrows 2K^+ + HPO_4^{2-}$$

$$KH_2PO_4 \rightleftarrows K^+ + H_2PO_4^- .$$

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Vandens struktūros kitimo tyrimas tirpaluose: H_2O-$CO(NH_2)_2$ – fosfatas (K_3PO_4, K_2HPO_4, KH_2PO_4) ultraakustiniu metodu

Reziumė

Ištirta, kaip veikia vandens struktūrą karbamidas ir kalio fosfatai, ištirpinti kartu ir atskirai. Vandens struktūros pakitimas tirtas ultraakustiniu ir densimetriniu metodu, matuojant ultragarso greitį bei tankį tirpaluose ir iš jų apskaičiuojant tirpalų adiabatinį spūdumą. Matavimai atlikti 25 °C temperatūroje. Karbamido koncentracija kito nuo 0 iki 15 mol/kg H_2O, nitratų koncentracija buvo 0,5 m.

Nustatyta, kad, didėjant karbamido koncentracijai, ultragarso greitis tirpaluose didėja, o adiabatinis spūdumas mažėja. Fosfatai padidina ultragarso greitį tirpaluose, o adiabatinį spūdumą sumažina. Didžiausią poveikį daro kalio fosfatas. Adiabatinio spūdumo sumažėjimą kalio fosfato tirpaluose sukelia susidaręs didelis vandens molekulių nespūdus poliarizacinis sluoksnis apie katijonus.

Iš adiabatinio spūdumo koeficientų apskaičiuotas ištirpintos druskos vienos molekulės nespūdus tūris ir dviejų druskų, ištirpintų kartu, vienos molekulės vidutinis nespūdus tūris. Apie vandens struktūros pokytį sprendžiama iš kartu ir atskirai ištirpintų dviejų druskų vienos molekulės vidutinio nespūdžiojo tūrio skirtumo Δv. Δv priklausomybę nuo karbamido koncentracijos galima paaiškinti fosfatų jonų hidratacijos pakitimu, didėjant karbamido koncentracijai.

Akustiniu metodu bandoma parodyti, kokios galimos kalio ortofosfatų disociacijos vandenyje.

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