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Investigation of the structure of carbamide and nitrate [KNO_3, $Cu(NO_3)_2$, $Zn(NO_3)_2$ $Mg(NO_3)_2$] water solutions applying ultraacoustic method

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Abstract

Carbamide [$CO(NH_2)_2$] is one of the best concentrated nitrogen fertilizers. Industrially it is produced by saturating nitrogen with carbon dioxide. Potassium nitrate (KNO_3) is a very important nitrate fertilizer. Nevertheless, fertilizing is not the only one field of utilization of potassium combinations. Combinations of potassium are indispensable composite parts of every human or living being cell. Magnesium as a bioelement goes into the composition of living material. It is an indispensable part of chlorophyll, which plays the main role in the process of photosynthesis. Copper is one of the bioelements too. As it is a catalizator of chemical processes inside cells, small amounts of it are indispensable for normal development of living beings and plants. In living beings copper is found mostly in liver. When human beings have copper deficiency (daily norm is 0.005 g for a person) weakness appears and anemia develops.

Zinc also plays an important role in biological processes. Small amounts of zinc are indispensable for growth and development of plants [1].

The usage of carbamide and nitrates in soil fertilization is not only an indispensable condition for a good harvest; through the plants it also gives all the necessary bioelements for the existence of living beings. Carbamide and potassium nitrates are used in the main or supplementary fertilizing of agricultural plants. Nitrates of magnesium, copper and zinc are used as microelements in compound fertilizers.

Water - carbamide solutions with dissolved organic and inorganic electrolytes in them were researched applying different methods and aims for different purposes by numerous authors. Combinations of carbamide with inorganic soils are described in a monography [2]. It is determined that dissolved carbamide destroys water structure [3]. Carbamide crystallic structure is being researched in the work [4], and system H_2O - $CO(NH_2)_2$ - Bu_4NBr is researched in the work [5].Viscosimetric properties of carbamide solvents are investigated in the work [6]. Water - carbamide solutions are investigated by nuclear magnetic resonance (NMR) in the work [7]. Investigations on the water - carbamide solutions are described in the works [8 - 12].

It can be stressed that works on properties of solutions of three components water - carbamide - nitrate are not numerous. The ultraacoustic method was mostly applied investigating two-member solutions [13 - 19]. The results of these investigations show that this method together with other methods gives us valuable knowledge about properties of solutions.

Aim of research

The change of water structure is investigated applying ultraacoustic method by measuring the ultrasound velocity in solutions and their adiabatic compression. Using ultraacoustic method, we can find uncompressive volume of one molecule of dissolved salt from the coefficients of adiabatic compression. If volume of the solution is V, and uncompressive volume in it is v_1, the uncompressive part in the solution is equal to:

$$\alpha = v_1/V \tag{1}$$

The uncompressive part of the solution volume can be calculated from the adiabatic compression coefficients of water and solution β_0 and β [20,21]:

$$\alpha = \Delta\beta/\beta_0 = v_1/V, \tag{2}$$

here $\Delta\beta = \beta_0 - \beta$.

From the formula (2) the uncompressive volume in the solution is equal to:

$$v_1 = (\Delta\beta/\beta_0)V \tag{3}$$

If salts of mass m_0 are dissolved in water, it has N molecules ($N = m_0N_A/\mu$, m_0 is the mass of salt, μ is the mole mass, N_A is the Avogadro's constant). The uncompressive volume for one molecule is

$$v = \Delta\beta V/(\beta_0 N) \tag{4}$$

Having denoted $n = N/V$ what is the concentration of molecules, we have:

$$v = \Delta\beta/(\beta_0 n) \tag{5}$$

There $n = m_0N_A\rho/(\mu m)$; there m_0 – is the mass of a dissolved salt, ρ - is the density of the solution, μ - is the molar mass of salt, m – is the mass of solution. If two substances are dissolved together, the average uncompressive volume is equal [22]:

$$v_v = \Delta\beta/[\beta_0(n_1 + n_2)] \tag{6}$$

There n_1 and n_2 are the concentrations of carbamide and nitrate molecules.

Uncompressive volume of salt molecule in a solution is made of cations and anions volume, which can be counted from their crystallographic radii. Cations are surrounded by uncompressive layer of polarized water molecules, and anions are not. Cations with a polarized water molecules layer can strengthen or weaken hydrogen connections between water molecules. This phenomena is called hydratation.

If ions enlarge hydrogen connections in ion molecules, hydratation is positive, if ions reduce the connections, hydratation is negative. Ion NO^-_3 does not destroy hydrogenic connections of water molecules [14]. The reason of solution adiabatic compression decrease with dissolved salt is ions uncompressive volume, water molecules polarization and hydratation. It also changes compression. Positive hydratation reduces compression of solution, and negative one increases it [22].

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

Change of 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:

$$\Delta V = \frac{\Delta\beta}{\beta_0(n_1+n_2)} - \frac{1}{2}\left(\frac{\Delta\beta_1}{\beta n_1} + \frac{\Delta\beta_2}{\beta_0 n_2}\right) \qquad (7)$$

There $\Delta\beta = \beta_0 - \beta$, β_0 – is the coefficient of water adiabatic compression, β - is the coefficient of carbamide and nitrate water solution, $\Delta\beta_1 = \beta_0 - \beta_1$, $\Delta\beta_2 = \beta_0 - \beta_2$, β_1 and β_2 – are the coefficients of adiabatic compressibility of carbamide and nitrate, while dissolving them separately, n_1 and n_2 – are the concentrations of carbamide and nitrate molecules.

The concentration of the adiabatic compressibility has been found from the formula [14]:

$$\beta = 1/(\rho c^2). \qquad (8)$$

Here ρ is the density of the solution; c is the speed of ultrasound in solution. The speed of ultrasound in solution is being measured by the ultraacoustic interferometer ($f = 2$ MHz) with uncertainty 0,01%. The density is being measured by the pyknometer ($V = 25$ cm^3) with uncertainty 0,001%.

Two-member systems were investigated: H_2O - $CO(NH_2)_2$, H_2O - nitrate, and three-member systems: H_2O - $CO(NH_2)_2$ - nitrate. The following nitrates were researched: KNO_3, $Cu(NO_3)_2$, $Zn(NO_3)_2$ and $Mg(NO_3)_2$.

Chemically especially clean salts have been used. Twice distilled water has been used for producing solutions. Water mass in solution is equal to 200 g. Concentration of carbamide changed from 0,5 to 15 mol/kg H_2O. Measurements were carried out of the temperature 25^{0}C.

Results of research and analysis

The concentrational interdependence in a system H_2O - $CO(NH_2)_2$ among ultrasound speed c, the coefficients of adiabatic compressibility β, uncompressive volume of one molecule v, while dissolving two salts, the difference of one molecule average uncompressive volume Δv, while dissolving salts together and separately while dissolving 0,5 m nitrate in a temperature of 25^{0}C is depicted graphically (fig. 1, 2, 3 and 4).

The dependence of ultrasound speed c upon concentration of carbamide at a temperature of 25^{0}C is depicted in the Fig.1. When the concentration of carbamide increases, ultrasound speed also increases. Besides, different nitrates have different influence on changes of ultrasound speed. It is connected with a charge of cation and its crystallographical radius, i.e. with its charge surface density. It was proved in research of other

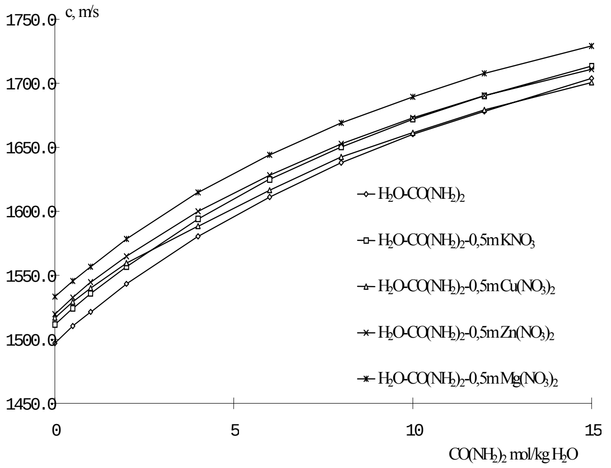

Fig.1.**Dependence of ultrasound speed c in a system H_2O - $CO(NH_2)_2$, while dissolving 0,5 m nitrates: KNO_3, $Cu(NO_3)_2$, $Zn(NO_3)_2$ and $Mg(NO_3)_2$, at a temperature of 25^{0}C**.

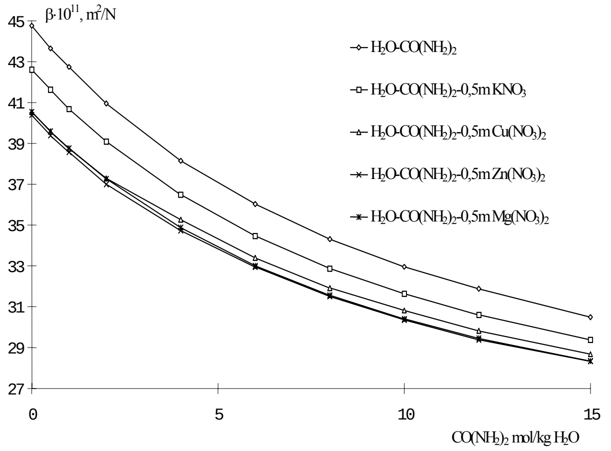

Fig.2.**Dependence of the coefficients of adiabatic compressibility β in a system H_2O - $CO(NH_2)_2$, while dissolving 0,5 m nitrates: KNO_3,, $Cu(NO_3)$, $Zn(NO_3)_2$ and $Mg(NO_3)_2$, at a temperature of 25^{0}C.**

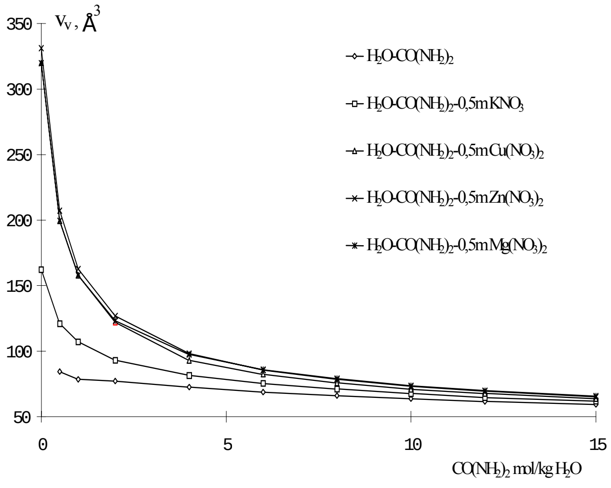

Fig.3.**Concentrational dependence of one molecule of average uncompressive volume of two dissolved salts in a system H_2O - $CO(NH_2)_2$, while dissolving 0,5 m nitrates: KNO_3. $Cu(NO_3)_2$, $Zn(NO_3)_2$ and $Mg(NO_3)_2$, at a temperature of 25^{0}C**.

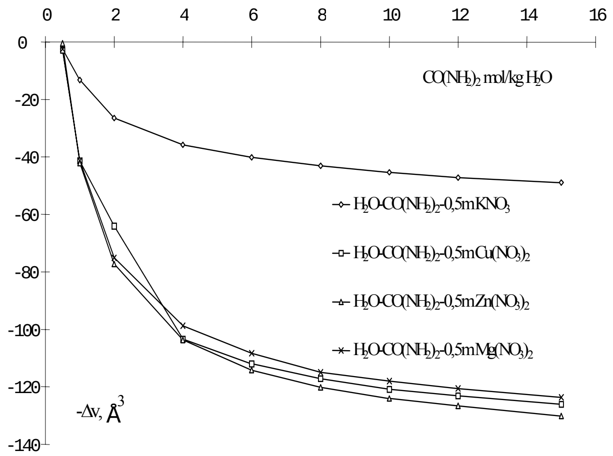

Fig.4.**Concentrational dependence of one molecule of two dissolved salts average uncompressive volume difference Δv, dissolving substances together and separately, in a system H_2O - $CO(NH_2)_2$, while dissolving 0,5 m nitrates: KNO_3, $Cu(NO_3)_2$, $Zn(NO_3)_2$ and $Mg(NO_3)_2$, at a temperature of 25^0C.**

systems [23,24]. The crystallographical radius of magnesium cation among researched nitrates is the least (*r* = 0,78*Å*), and its influence in the changes of ultrasound speed is the greatest.

In Fig.2 the dependence of the adiabatic compression coefficient β upon the concentration of carbamide at a temperature of 25^0C is performed. When concentration of carbamide increases, adiabatic compression lessens. Magnesium nitrate reduces adiabatic compression mostly. Zinc and copper nitrates are not much behind.

In Fig.3 uncompressive volumes of nitrates when concentration of carbamide is 0, and concentration of one carbamide molecule in water solution, are given. It can be seen from Curve 1 that, when the concentration of carbamide increases, the uncompressive volume of one molecule decreases insignificantly. It proves, that molecules of carbamide also change compressibility of water molecules insignificantly. In our opinion, when concentration of carbamide is 15 mol/kg H_2O, the uncompressive volume of carbamide molecule is equal (or very near) to its crystallographic volume. This volume is equal to 59,3$Å^3$. Then crystallographic radius of carbamide molecule would be equal to: r = 2,42*Å*.

Average uncompressive volume of nitrates molecules considerably lessens, while concentration of carbamide increases to 6 mol/kg H_2O; after that it changes inconsiderably. In our opinion, carbamide dissolved in water destroys uncompressive volume of nitrates. In their turn, cations lose hydratation. A new structure of solution is formed. Data on one molecule average uncompressive crystallographic volume and volume that is counted from research data of carbamide and nitrates are presented in Table 1.

Ion NO^-_3 volume is equal to 24,8$Å^3$ [25]. Crystallographic radii of cations are taken according to Goldschmidt [26]. Not large declinations are got comparing average uncompressive crystallographic volumes of carbamide and nitrates with average uncompressive experimental volumes, that are got from the above mentioned salts, when concentration of carbamide is 15 mol/kg H_2O, and concentration of nitrate is 0,5 m. Those declinations make only about one third of water molecule volume. It follows, that our proposition that carbamide dissolved in water destroys average water molecules volume of nitrates cations is correct.

Table 1. **Comparing of theoretical and experimental meanings of carbamide and nitrates one molecule average uncompressive volume. Volume of an anion NO^-_3. $v_0 = 24{,}8Å^3$ [25], crystallographic volume of carbamide mol. $v_k = 59{,}3Å^3$**

No	Nitrates	KNO_3	$Cu(NO_3)_2$	$Zn(NO_3)_2$	$Mg(NO_3)_2$
1	Crystallographic radius of a cation r_k, *Å*	1,33	0,79	0,83	0,78
2	Uncompressive crystallographical volume of one nitrate molecule v_k, $Å^3$($v_k = 4/3\pi r^3_k + nv_0$, n - number of anions in a molecule)	34,65	51,66	51,99	51,59
3	Average crystallographic volume $v_{vk} =(v_k + v_n)/2$ of carbamide v_k and nitrate v_n one molecule, $Å^3$	47,00	55,48	55,65	55,45
4	Average uncompressive volume v_v, of carbamide and nitrate dissolved together one molecule, when concentration of carbamide is 15 mol/kg H_2O and concentration of nitrate is 0,5 m, $Å^3$ (3)	61,92	63,61	65,07	65,74
5	Average uncompressive volume v_v of carbamide and nitrate dissolved separately one molecule when concentration of carbamide is 15 mol/kg H_2O and concentration of nitrate is 0,5 m, $Å^3$, $v_v = 0{,}5[\Delta\beta_1/(\beta_0 n_1) + \Delta\beta_2/(\beta_0 n_2)]$	110,85	189,67	195,2	189,5
6	Difference of carbamide and nitrate one molecule average uncompressive volume while dissolving substances together and separately, Δv, $Å^3$ (4)	-48,93	-126,1	-130,1	-123,77
7	Difference between average uncompressive volume of carbamide and nitrate one molecule while dissolving substances together, when concentration of carbamide is 15 mol/kg H_2O and concentration of nitrate is 0,5 m, and crystallographic volume, Δv_1, $Å^3$, $\Delta v_1 = v_v - v_{vk}$	14,92	8,13	9,42	10,29

In Fig.4 the dependence of one molecule of dissolved two salts average uncompressive volume difference Δv is almost independent of concentration. It can be affirmed that nitrate dissolved separately has a large volume of uncompressive water molecules, and dissolved together with carbamide loses uncompressive volume of water molecules, and, due to this, a large difference of uncompressive volumes, dissolving salts together and separately is formed.

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Ultraakustinis karbamido ir nitratų [KNO_3, $Cu(NO_3)_2$, $Zn(NO_3)_2$ ir $Mg(NO_3)_2$] vandeninių tirpalų struktūros tyrimas

Reziumė

Ištirta, kaip vandens struktūrą veikia karbamidas ir nitratai, ištirpinti kartu ir atskirai. Vandens struktūros pakitimas tirtas ultraakustiniu metodu, matuojant ultragarso greitį tirpaluose ir jų adiabatinį spūdumą. Iš adiabatinio spūdumo koeficientų apskaičiuotas ištirpintos druskos vienos molekulės nespūdusis tūris ir dviejų druskų, ištirpintų kartu, vienos molekulės vidutinis nespūdusis tūris. Vandens struktūros pokytis apskaičiuotas iš kartu ir atskirai ištirpintų dviejų druskų vienos molekulės vidutinio nespūdžiojo tūrio skirtumo. Matavimai atlikti 25°C temperatūroje. Karbamido koncentracija kito 0,5-15 mol/kg H_2O intervale, nitratų koncentracija buvo 0,5 m.

Tyrimais nustatyta, kad karbamidas ir nitratai ultragarso greitį tirpale padidina, o adiabatinį spūdumą sumažina, ir šis poveikis didėja, didėjant karbamido koncentracijai. Apskaičiavus nitratų ir karbamido vienos molekulės nespūdžiuosius tūrius vandenyje ir jų priklausomybę nuo karbamido koncentracijos, taip pat kartu ir atskirai ištirpintų dviejų, druskų vienos molekulės vidutinio nespūdžiojo tūrio skirtumą konstatuojama, kad karbamidas, ištirpintas vandenyje, dėl susidariusios naujos tirpalo struktūros suardo nitratų katijonų nespūdųjį vandens molekulių tūrį.

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