Investigation of water structure changes in carbamide and nitrates [$NaNO_3$, $Ca(NO_3)_2$, NH_4NO_3] solutions by ultraacoustic method

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Carbamide or urea is the final product of an albumen metabolism of a human being and majority of mammalia. It is produced in liver. It is found in blood, muscles and other tissues, in saliva, lymph and milk. Carbamide regulates water metabolism in an organism an hydratation of tissues. Microorganisms of alimentary canal of ruminant animals use carbamide in biosynthesis of albumen. Carbamide is used in chemical industry for production of formaldehyde resins, medicine, hydrazine, hydrazoformamide, melanine, some sorts of paints and for synthesizing of other combinations, for oil deparaffination and stabilization of smokeless powder. Toothpastes and cosmetical creams contain carbamide too. Carbamide is one of the best concentrated nitrogen fertilizers. In industry carbamide is produced from ammonium hydrate and carbon dioxide. The most usual form of this material - granules. Carbamide is used in the main and supplementary fertilization of crops. Nitrates of natrium, calcium and ammonium are also used as nitrogen fertilizers. Complex fertilizers, e. i., mixtures of various fertilizers, are widely used nowadays. The aim of our work is to investigate the influence of carbamide and natrium, calcium and ammonium nitrates on water structure, while dissolving them separately and together at the temperature of 25, 30, 40^0 C, at the concentration of nitrates 0,5 m (0,5 substance of mole per 1 kg H_2O), and changing concentration of carbamide at intervals from 0,5 to 15 mol/kg.

Water is compressive but uncompressive particles - ions - appear after dissolving of salts.

Ions influence water molecules and hydrogen connections between molecules, they can weaken or strengthen the connections, and that is the reason why compression of solution changes.

If volume of the solution is V, and uncompressive volume in it is v_1 , the uncompressive part in the solution is equal to:

$$\alpha = \frac{v_1}{V}. \quad (1)$$

The uncompressive part of the solution volume can be calculated from the adiabatic compression coefficients of water and solution β_0 and β [1 - 10]:

$$\alpha = \frac{\Delta\beta}{\beta_o} = \frac{v_1}{V}\ , \quad (2)$$

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

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

$$v_1 = \frac{\Delta\beta}{\beta_o}V. \quad (3)$$

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

$$V_v = \frac{\Delta\beta V}{\beta_o N} \quad (4)$$

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

$$V_v = \frac{\Delta\beta}{\beta_o n}. \quad (5)$$

If two salts instead of one are dissolved in the solution, the average uncompressive volume in the solution for one molecule is equal to:

$$V_v = \frac{\Delta\beta}{\beta_o\left(n_1 + n_2\right)}. \quad (6)$$

Here $\Delta\beta=\beta_o-\beta$, β_o is the coefficient of the adiabatic compression of water, β is the coefficient of the adiabatic compression of carbamide and nitrate solution, n_1 and n_2 - concentrations of carbamide and nitrate molecules.

An average uncompressive volume per one molecule when carbamide and nitrate are dissolved separately, is equal to:

$$V_v = \frac{1}{2}\left(V_{v_1} + V_{v_2}\right), \quad (7)$$

where V_{v_1} is the uncompressive volume of one molecule of carbamide, when dissolved separately, V_{v_2} is an uncompressive volume of one molecule of nitrate, when dissolved in water separately.

The evaluation of changes of water structure is based on the difference of an average uncompressive volume of one molecule, when the substances are dissolved together and separately:

$$\Delta V = \frac{\Delta\beta}{\beta_o\left(n_1+n_2\right)} - \frac{1}{2}\left(\frac{\Delta\beta_1}{\beta_o n_1} + \frac{\Delta\beta_2}{\beta_o n_2}\right), \qquad (8)$$

where $\Delta\beta_1=\beta_o-\beta_1$; $\Delta\beta_2=\beta_o-\beta_2$, β_1 and β_2 are the adiabatic compression coefficients of carbamide and nitrate, dissolved separately.

The coefficients of the adiabatic compression (β_o, β, β_1, β_2) have been evaluated by the ultraacoustic method according to the formula $\beta=1/(\rho v^2)$. Here ρ is the density of the solution, v is the speed of ultrasound in the solution. The speed of ultrasound has been measured by the ultrasound interferometer to within 0.01% (v=2 MHz). The density has been measured by a pyknometer to within 0.001% (volume of the pyknometer is 25 cm^3). The volume of the solution has been calculated by the formula $V=m/\rho$ where m is the mass of the solution, ρ is its density.

The uncompressive part of the solution v_1 consists of ions (cations and anions). The volume of these ions can be calculated from their crystallographic radius. Cations of nitrates are surrounded with two layers of water molecules of different structures [11]. Anions have only one water molecules' layer of different structure, exept NO_3^- , which does not destroy water structure at all [7, 12, 13, 14]. Water molecules, which are in the first layer around the cation, are only polarized and deformed [11,13]. The dispersive Van der Waals forces appear as a result of deformation. These forces destroy hydrogen connections of water molecules. This phenomenon is called hydratation. Ions of some salts strengthen hydrogen connections between water molecules, what is a positive hydratation, while other ions weaken hydrogen connections between water molecules and that is called a negative hydratation. A water compressibility decreases when the hydratation is positive, and increases when the hydratation is negative [11]. The uncompressive volume of ions themselves must not be dependent neither from concentration of salts nor from a temperature. The polarization layer of cations has to increase when temperature increases, as the Debay

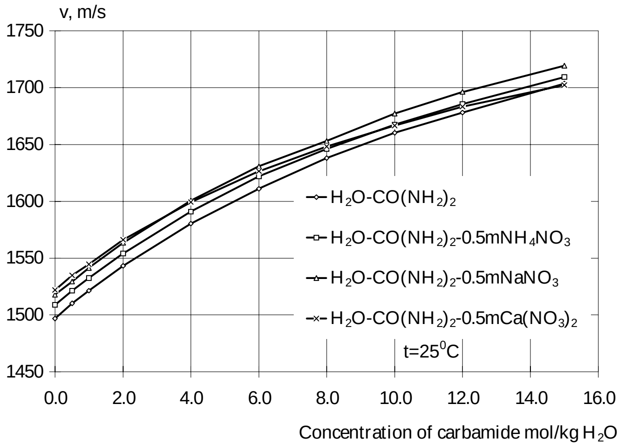

Fig.1. Dependence of ultrasound *v* on the concentration of carbamide at te temperature of 25°C

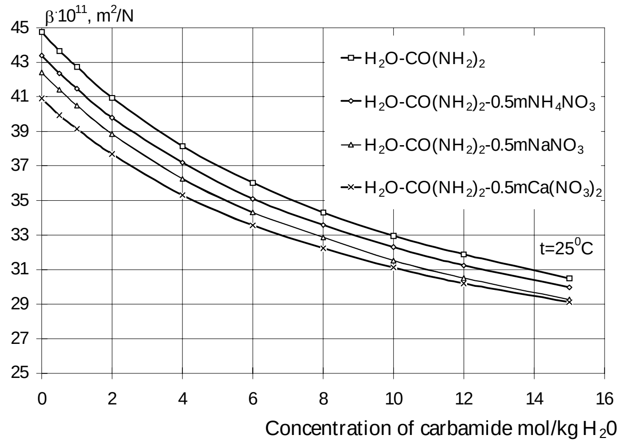

Fig. 2. Dependence of the coefficient of adiabatical compressibility of the solution on the concentration of carbamide at the temperature of 25° C.

screening radius is directly proportional to a square root from absolute temperature [15].

Carbamide destroys water structure [16–19] and forms more compact combinations with water molecules, therefore, the adiabatic compressibility of the solution decreases, and the speed of ultrasound increases. Carbamide, as an organic substance, can have different influence on hydrogen connections from that of nitrate ions can. Thus, the process of hydratation is a complicated one. In our opinion, the different ΔV when salts are dissolved together or separately occurs only because of changes in hydratation process.

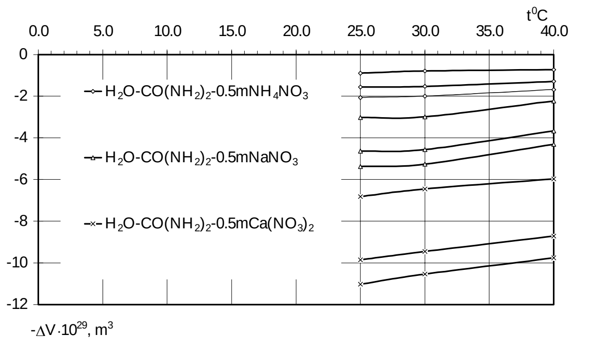

Fig. 4**. Dependence of ΔV on the temperature, when concentration of the solution is 2, 6 and 12 mol/kg**

The dependence of v and β on the concentration of carbamide and the dependence of ΔV on temperature and on the concentration of carbamide is depicted in Fig. 1, 2, 3 and 4.

In the Fig. 1 the dependence of ultrasound speed v on the concentration of carbamide is shown. We see, that at the increasing concentration of carbamide, the ultrasound velocity increases also. The ultrasound velocity is increased by nitrates in the solution, and sodium nitrate is of the strongest influence here.

The Fig.2 shows the dependence of the solutions' adiabatic compressibility coefficient β on the concentration of carbamide. We see that at the increasing concentration of carbamide, the adiabatic compressibility of solutions decreases. Tbe adiabatic compressibility of solutions is decreased by nitrates, and calcium nitrate is of the strongest influence.

The dependence of ΔV on the concentration of carbamide is shown in Fig. 3. The graph shows that if concentration of carbamide increases, ΔV decreases. When the concentration of carbamide exceeds 10 mol/kg, ΔV almost does not change. It means the change of hydratation to be very small as the number of free water molecules is small.

Fig. 4 presents the dependence of ΔV on a temperature at different carbamide concentrations. It is clear that when a temperature increases, ΔV also increases. This dependency of ΔV is not related to the concentration of carbamide. It is possible that the change of hydratation process increases at the increasing temperature.

References

1. **Ïàñèíñêèé À.Ã.** Ñæèìàåìîñòü è ñîëüâàòàöèÿ ðàñòâîðîâ ýëåêòðîëèòîâ. // ÆÔÕ¸ 1938, ò.11,â.5, 606-627.
2. **Äóáèíèíà Å.Ô., Êóäðÿâöåâ Á.Á.** Ñêîðîñòü ðàñïðîñòðàíåíèÿ óëüòðàçâóêà è ãèäðàòàöèÿ ðàñòâîðîâ. // ÆÔÕ, 1957, ò.31, â.10, 2191-2199.
3. **Ìèõàéëîâ È.Ã., Ñîëîâüåâ Â.À.** Îñíîâû ìîëåêóëÿðíîé àêóñòèêè. Ì.:Íàóêà,1964.
4. **Ñòþýð Äæ., Åãåð Å.** Ñâîéñòâà ãàçîâ, æèäêîñòåé è ðàñòâîðîâ. Ïîä ðåä. Ó.Ìåçîíà. Ì.: Ìèð, 1969, 375-379.
5. **Ðîáèíñîí Ð., Ñòîêñ Ð.** Ðàñòâîðû ýëåêòðîëèòîâ. Ì.:èë, 1963.
6. Íåêîòîðûå ïðîáëåìû ñîâðåìåííîé ýëåêòðîõèìèè. Ïåð. ñ àíãë., ïîä ðåä. Äæ.Áîêðèñà.
7. **Ìèõàéëîâ È.Ã., Ñàâèíà Ë.È.** è äð. Ñêîðîñòü çâóêà è ñæèìàåìîñòü êîíöåíòðèðîâàííûõ ðàñòâîðîâ ñèëüíûõ ýëåêòðîëèòîâ. // Âåñòí.ËÃÓ,1957, â. 22, 25-42.
8. **Ïîíîìàðåâ Â.Ê.** Èññëåäîâàíèå ãèäðàòàöèè ýëåêòðîëèòîâ óëüòðààêóñòè÷åñêèì ìåòîäîì. // ÆÔÕ, 1979, ò.53, N 4, ñ. 963-965.
9. **Ïîíîìàðåâ Â.Ê.** Ïðèìåíåíèå óëüòðààêóñòè÷åñêîãî è êèíåìàòè÷åñêîãî ìåòîäà äëÿ èçó÷åíèÿ ãèäðàòàöèè ýëåêòðîëèòîâ. // ÆÔÕ, ò. 52, N 6, 1462-1465.
10. **Ïîíîìàðåâ Â.Ê.** Îïðåäåëåíèå ÷èñåë ãèäðàòàöèè èîíîâ ïî êîýôôèöèåíòàì ñæèìàåìîñòè è âÿçêîñòè. // Õèìèÿ è õèìè÷åñêàÿ òåõíîëîãèÿ. Ò. 21, â. 6, 826-830.
11. **Janënas V. K.** Nitratø hidratacijos tyrimas ultraakustiniu metodu. // Ultragarsas. K.: Technologija. 1966, Nr. 1.
12. **Ëèïëàâêîâà È.È.** Óðàíèë è åãî ñîåäèíåíèÿ. Ì.: ÀÍ ÑÑÑÐ¸ 1959¸ 250-254.
13. **Õîðí Ð.** Ìîðñêàÿ õèìèÿ. Ì.: Ìèð 1972.
14. **Janz J., James D. W.** // Elektrochim. Acta, 1962, vol. 7, p. 427.
15. Õèìè÷åñêàÿ ýíöèêëîïåäèÿ. Ì.: 1990, òîì 2, ñ. 7.
16. **Frank S., Franks F..** Structural approch to the solvent power of water for hydracarbons; urea as a structure breaker // J. Chem. Phys., 1968, 48, 10, 4746-4757.
17. **Hammes G.G., Schimmel P.R.** An investigation of water-urea and water-polyethylen glycol interaction // Journal of the American Chemical Society /89:2/, January 18, 1967, 442-446.
18. **Beauregard D.V., Barett R.E.** Ultrasonics and water structure in urea solutions //J. Chem. Phys., 1968, 49, 12, 5241-5244.
19. **Herskovits T.T., Kelly T.M.** Viscosity studies of aqueous urea solution // J. Amer. Chem. Soc., 1972, 94, 13, p. 4424.

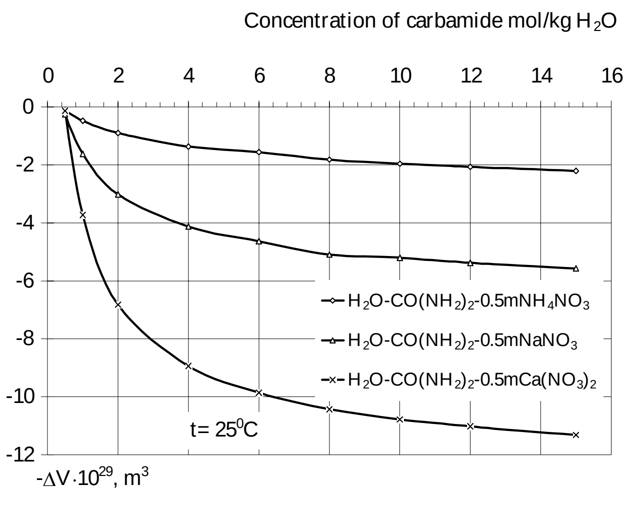

Fig. 3**. Dependence of ΔV on the concentration of carbamide at the temperature of 25° C.**

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Vandens struktûros pokyèiø tyrimas karbamido ir nitratø [$NaNO_3$, $Ca(NO_3)_2$, NH_4NO_3] tirpaluose ultraakustiniu metodu

Reziumë

Iðtirta, kaip vandens struktûrà veikia karbamido ir natrio, kalcio bei amonio nitratai, iðtirpinti kartu ir atskirai, esant 25, 30 ir 40°C temperatûrai. Nitratø koncentracija buvo 0.5 mol/kg, o karbamido koncentracija buvo keièiama 0.5-15 mol/kg intervale. Vandens struktûros pokytis ávertintas remiantis vienos molekulës vidutinio nespûdaus tûrio skirtumu ΔV, iðtirpinus medþiagas kartu ir atskirai. Nustatyta, kad kai karbamido koncentracija didesnë nei 10 mol/kg, ΔV beveik nekinta. Tai rodo, kad, esant didesnei karbamido koncentracijai, vandens struktûra jau nebekinta.