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Estimation of changes in water structure dissolving salts in water applying acoustic and viscosimetric methods

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Changes in water structure dissolving salts can be estimated applying not only ultraacoustic, but also the viscosimetric method.

The influence of two nitrates [$NaNO_3$ and $Ca(NO_3)_2$; $NaNO_3$ and NH_4NO_3] on a water structure, when nitrates are dissolved together and separately at the temperature of 25 and 30^0 C, and concentration of the solution is 0,5 m (0,5 moles of salt in 1 kg of water), is investigated in this article [1]. The change in water structure is estimated from the difference of an average uncompressive volume of two salts dissolved together and separately. The uncompressive volume is calculated from the coefficients of the adiabatic compressibility β in solutions, that are found applying ultraacoustic and viscosimetric methods. The speed of ultrasound was measured by an ultrasound interferometer ($f = 10MHz$). Error of measurement is 0,02%. The density in solutions was measured by a pyknometer (volume 50 cm^3), and error of measurements is 0,001%. Bidistillation was used in making solutions. Salts were chemically cleaned (grade ХЧ and ЧДА). The temperature of thermostating was measured in within $0{,}05^0$ C. The adiabatic compressibility in solutions was evaluated from the formula [1,2]:

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

here ρ is the density of a solution, c is the speed of ultrasound in a solution. Error of adiabatic the compressibility is 0,08%.

At first we estimate changes in water structure from the difference of the average uncompressive volume Δv, dissolving one molecule of two salts together and separately. Δv is counted from the data that is obtained applying acoustic method.

$$\Delta v = v_v - v_1', \tag{2}$$

here v_v is the average uncompressive volume of one molecule, when salts are dissolved together.

$$v_v = \frac{\Delta\beta}{\beta_0 (n_1 + n_2)}, \tag{3}$$

here $\Delta\beta=\beta_0-\beta$; β_0 is the adiabatic compressibility of water, β is the adiabatic compressibility of solution, when salts are dissolved together, n_1 and n_2 are the number of molecules of dissolved salts in a unit of volume of the solution, v_1' is the average uncompressive volume of one molecule, when salts are dissolved separately:

$$v_v' = ½ (v_1 + v_2), \tag{4}$$

where v_1 and v_2 are the uncompressive volumes of molecules in the both salts:

$$v_1 = \frac{\Delta\beta_1}{\beta_0 n_1} \tag{5}$$

and

$$v_2 = \frac{\Delta\beta_2}{\beta_0 n_2}, \tag{6}$$

Inserting (5) and (6) in the Eq. (4), we obtain:

$$v_1' = \frac{1}{2}\left(\frac{\Delta\beta_1}{\beta_0 n_1} + \frac{\Delta\beta_2}{\beta_0 n_2}\right), \tag{7}$$

here $\Delta\beta_1=\beta_0-\beta_1$; $\Delta\beta_2=\beta_0-\beta_2$; β_1 and β_2 are the adiabatic compressibilities of salts dissolved separately in water.

After inserting the meanings of v_v and v_v' from (3) and (7) in the Eq. (2), we obtain:

$$\Delta v = \frac{\Delta\beta}{\beta_0 (n_1 + n_2)} - \frac{1}{2}\left(\frac{\Delta\beta_1}{\beta_0 n_1} + \frac{\Delta\beta_2}{\beta_0 n_2}\right). \tag{8}$$

The uncompressive part of a solution can also be found from coefficients of a solvent and dynamic viscosity of the solution, using the Einstein equation [3,4,5]:

$$\eta/\eta_0 = 1 + 2.5\alpha, \tag{9}$$

here η and η_0 are the coefficients of dynamic viscosity of the solution and solvent, α is the uncompressive part in the solution: $\alpha = v/V$, v is the uncompressive volume in the solution, V - volume of the solution.

From the Eq. (9)

$$\alpha = \frac{\Delta\eta}{2.5\eta_0}, \tag{10}$$

where $\Delta\eta=\eta-\eta_0$.

The uncompressive part of the solution can be expressed in the following way [5]:

$$\alpha = \frac{v}{V} = \frac{\Delta\eta}{2.5\eta_0} = \frac{N \cdot v}{V} = n v_v, \tag{11}$$

where N is the number of molecules in dissolved salt, v_v is the uncompressive volume of one molecule in salt, n is the number of salt molecules in a unit of the volume of solution:

$$n = \frac{N}{V} = \frac{\frac{m_0}{M} N_A}{V} = \frac{m_0 \rho N_A}{Mm}, \tag{12}$$

where m_0 is the mass of dissolved salt, N_A is the Avogadro constant, M is the moles mass of salt, m is the mass of solution.

From the Eq. (11) the uncompressive volume of one salt molecule is equal:

$$v_v = \frac{\Delta\eta}{2.5\eta_0 n}. \tag{13}$$

While dissolving two salts, the average uncompressive volume of one molecule is found from the formula:

$$v_v = \frac{\Delta\eta}{2.5\eta_0\left(n_1 + n_2\right)}. \qquad (14)$$

The change of water structure is estimated from the difference of the average uncompressive volume of one molecule in two salts dissolved together and separately:

$$\Delta v = \frac{\Delta\eta}{2.5\eta_0\left(n_1 + n_2\right)} - \frac{1}{2}\left(\frac{\Delta\eta_1}{2.5\eta_0 n_1} + \frac{\Delta\eta_2}{2.5\eta_0 n_2}\right), \qquad (15)$$

here $\Delta\eta=\eta-\eta_0$; η_0 is the coefficient of dynamic viscosity in water, η is the coefficient of dynamic viscosity in solution, when both salts are dissolved; $\Delta\eta_1=\eta_1-\eta_0$ and $\Delta\eta_2=\eta_2-\eta_0$; η_1 and η_2 are the coefficients of the dynamic viscosity of salts dissolved separately in water. The viscosity of solutions was measured by the Ostwald viscosimeter, at temperatures of 25 and 30^0 C, the error is 1%.

Table 1. **Values of coefficients of the density •, adiabatic compressibility • and dynamic viscosity • in water and nitrates aquatic solutions at temperatures of 25 and 30^0 C**

System	t^0 C	$\rho.10^{-3}$, kg/m^3	c, m/s	$\beta.10^{11}$, m^2/N	$\eta.10^3$, Pa.s
H_2O-0,5m $NaNO_3$	25	1,0236	1517,80	42,41	0,915
	30	1,0223	1529,00	41,84	0,818
H_2O-0,5m $Ca(NO_3)_2$	25	1,0550	1522,05	40,91	0,970
	30	1,0526	1532,00	40,47	0,904
H_2O-0,5m NH_4NO_3	25	1,0125	1508,89	43,38	0,884
	30	1,0110	1520,56	42,78	0,785
H_2O [7]	25	0,99707	1497,00	44,75	0,8937
	30	0,99567	1509,44	44,08	0,8007

Table 2. **Values of the density •, speed of ultrasound *c*, coefficient of adiabatic compressibility •, average uncompressive volume v_v of one molecule, difference of average uncompressive volume of one molecule •*v*, when nitrates are dissolved together and separately in three-member system H_2O-0,5m $NaNO_3$-0,5m NH_4NO_3 at temperatures of 25 and 30^0 C**

t^0C	$\rho.10^{-3}$, kg/m^3	c, m/s	$\beta.10^{11}$, m^2/N	v_v, Å^3	v_1', Å^3	•v, Å^3
25	1,03629	1529,90	41,23	136,52	153,52	-16,64
30	1,03478	1540,38	40,73	132,04	139,53	-7,49

Table 3. **Values of the density •, speed of ultrasound c, coefficient of adiabatic compressibility •, average uncompressive volume v_v of one molecule, when nitrates are dissolved together and separately v_1', difference of average uncompressive volume of one molecule •v, when nitrates are dissolved together and separately in three-member system H_2O-0,5m $NaNO_3$-0,5m $Ca(NO_3)$ at temperatures of 25 and 30^0 C**

t^0C	$\rho.10^{-3}$, kg/m^3	c, m/s	$\beta.10^{11}$, m^2/N	v_v, Å^3	v_1', Å^3	•v, Å^3
25	1,08017	1544,22	38,82	229,07	238,74	-9,67
30	1,07599	1552,56	38,56	216,95	230,34	-13,39

Table 4. **Values of the coefficient of dynamic viscosity •, average uncompressive volume of one molecule v_v when nitrates are dissolved together and separately v_1', difference of average uncompressive volume of one molecule •v, when nitrates are dissolved together and separately in three-member system H_2O-0,5m $NaNO_3$-0,5m NH_4NO_3 at temperatures of 25 and 30^0 C**

t^0C	$\eta.10^3$, Pa.s	v_v, Å^3	v_1', Å^3	•v, Å^3
25	0,8848	-7,14	9,704	-16,84
30	0,7915	-7,984	6,54	-14,52

Table 5. **Values of the coefficient of dynamic viscosity •, average uncompressive volume of one molecule v_v when nitrates are dissolved together and separately v_1', difference of average uncompressive volume of one molecule •v, when nitrates are dissolved together and separately in three-member system H_2O-0,5m $NaNO_3$-0,5m $Ca(NO_3)$ at temperatures of 25 and 30^0 C**

t^0C	$\eta.10^3$, Pa.s	v_v, Å^3	v_1', Å^3	•v, Å^3
25	1,0165	83,27	99,4	-16,13
30	0,8779	66,93	102,905	-35,97

Data about density ρ, speed of ultrasound c, adiabatic compressibility β and dynamic viscosity η in two-member system water-nitrate at a temperature of 25 and 30^0 C are given in Table 1. Data about an uncompressive volume v of one molecule and the difference Δv between uncompressive volumes of one molecule, when both nitrates are dissolved together and separately and are obtained from measurements of a dynamic viscosity are given in Tables 2 and 3. Analogic data obtained from measurements of a dynamic viscosity are presented in Tables 4 and 5.While comparing data of Tables 2 and 3 with measurement results in Tables 4 and 5, we see, that counting meanings in measurements differ according to acoustic and viscosimetric data, however the motion is the same. Thus, we can estimate changes in water structure from coefficients of dynamic viscosity in solutions dissolving salts in water. Simply the acoustic method is about 10 times more exact than viscosimetric method. The quantity Δv is negative for the reason that salts, dissolved separately have a larger hydrating influence, than in the case when they are dissolved together. When salts are dissolved separately, there are more free water molecules than dissolving together. The Table 4 presents average uncompressive volume v_v of one salt molecule, that is calculated from Eg. (14) and that is negative and value of volume is small. It occurs for the reason that ammonium nitrate lessens the viscosity of solution. Ammonium nitrate, dissolved in water, lessens the viscosity of solution too [6]. In our opinion, the use of Eq. (13) for calculated of the uncompressive volume of one salt molecule with the help of the coefficients of dynamic viscosity, is snitable only for the salts that increase the viscosity of a solution, and is not snitable to those that lessen the viscosity of a solution, because of a negative and unreal calculated value.

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Vandens struktūros pokyčio vandeniniuose druskų tirpaluose nustatymas akustiniu ir viskozimetriniu metodais

Reziumė

Darbe parodyta, kad vandens struktūros pokytį, ištirpinus druskas, galima nustatyti ne tik ultraakustiniu, bet ir viskozimetriniu metodu. Ištirtas dviejų nitratų [$NaNO_3$ bei $Ca(NO_3)_2$ ir $NaNO_3$ bei NH_4NO_3], ištirpintų kartu ir atskirai 25 ir 30^0 C temperatūroje, poveikis vandens struktūrai, esant tirpalų koncentracijai 0,5 m. Vandens struktūros pokytis pradžioje nustatytas iš kartu ir atskirai ištirpintų dviejų druskų vidutinio nespūdžiojo tūrio, tenkančio vienai molekulei, skirtumo Vienai druskos molekulei tenkantis vidutinis nespūdusis tūris apskaičiuotas remiantis akustiniu metodu gautais duomenimis.

Antroje darbo dalyje tie patys skaičiavimai atlikti naudojantis tirpiklio ir tirpalo dinaminės klampos koeficientais. Palyginus gautus rezultatus, padaryta išvada, kad akustinis metodas apie 10 kartų tikslesnis už viskozimetrinį metodą. Be to, nustatyta, kad viskozimetrinis metodas, taikomas vienai molekulei tenkančiam vidutinio nespūdžiajam tūriui apskaičiuoti, netinka druskoms, kurios mažina tirpiklio klampą.

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