T. Yakhno, V. Yakhno

The mechanism of "water activation". Water phases at room conditions.

**Federal Research Center Institute of Applied Physics of the Russian Academy of Sciences
(IAP RAS), Nizhny Novgorod 603950, Russia**

**N. I. Lobachevsky State University of Nizhny Novgorod (National Research University),
Nizhny Novgorod 603950, Russia**

**Correspondence: yakhta13@gmail.com (TY); yakhno@appl.sci-nnov.ru (VY)**

**Conference "Physics of aqueous solutions"
Moscow, December 20-22, 2021**

Dear colleagues,

Everyone has known since school times that water is a universal solvent. This means that any substance, in contact with water, leaves its own "material trace" in it, which depends on the nature of the given substance. This applies both to the air environment and to the material of the vessel in which it is placed. That is, in the world around us, in principle, "chemically pure" water cannot exist. According to the National Institutes of Health, none of the current water treatment methods are perfect. https://www.orf.od.nih.gov/TechnicalResources/Documents/DTR%20White%20Papers/Laboratory%20Water-Its%20Importance%20and%20Application-March-2013_508.pdf). This fact is ignored by most of the authors of scientific works. In this communication, we will show the microstructure of real water, which we described earlier, and demonstrate the role of its microdispersed phase in the "activation" mechanism [1-4].

1. T. Yakhno, V. Yakhno. A study of structural organization of water and aqueous solutions by means of optical microscopy. // Crystals, 2019, 9(1), 52. DOI:10.3390/cryst9010052 http://www.mdpi.com/2073-4352/9/1/52/pdf
2. T. Yakhno, M. Drozdov, V. Yakhno,. Giant Water Clusters: Where Are They From? // Int. J. Mol. Sci. 2019, 20, 1582; doi:10.3390/ijms20071582. https://www.mdpi.com/1422-0067/20/7/1582/pdf
3. T. Yakhno, V. Yakhno. Study of the role of the microdispersed phase of water during its transition to the state of activation. Topical issues of biological physics and chemistry, 2020, Vol. 5, No. 1, p. 43-51.(In Russ.)
4. T. Yakhno, V. Yakhno. Water as a microdispersed system. Water "activation" mechanism. Water phases at room conditions. Review. To be published in WATER Journal in March, 2022.

In accordance with our data based on optical microscopy, water of any degree of purification is a microdisperse system.

| Clear glass (substrate)	Distilled water	Tap water
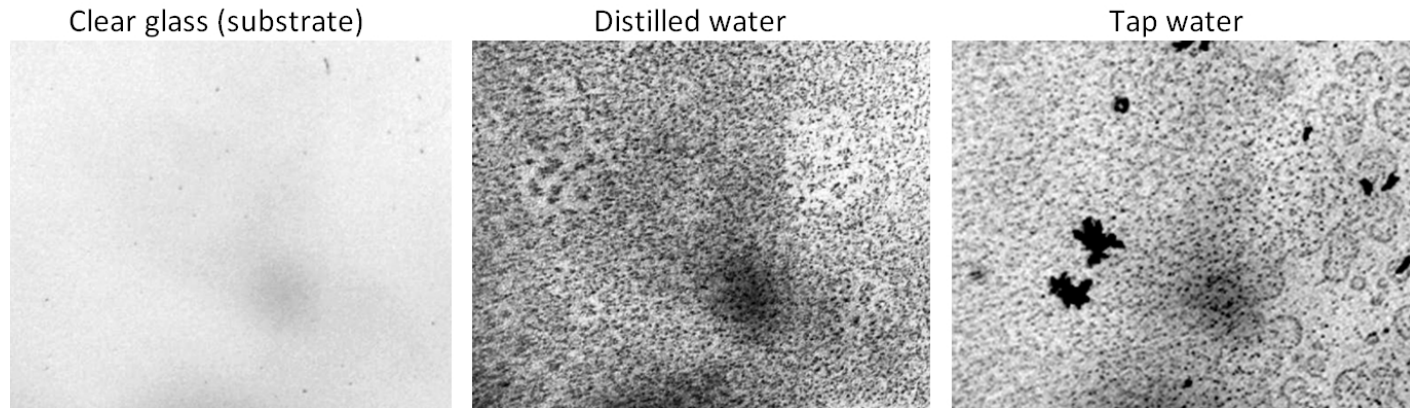
From left to right: empty glass (backing), distilled water, tap water. The thickness of the liquid layer between the slide and the cover glass is 8 microns. The width of each frame is 1.5 mm
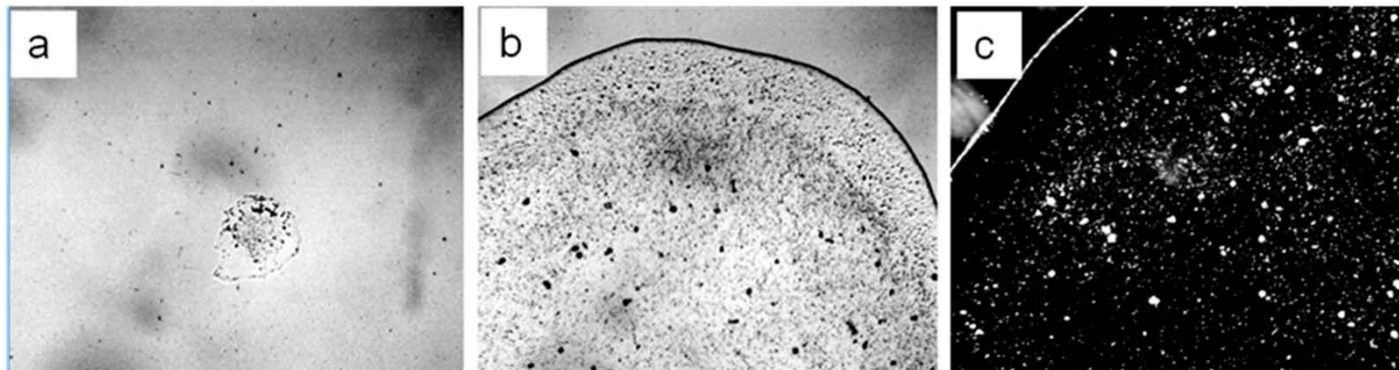
Sediment after drying a drop of distilled water with a volume of 3 µL on a glass substrate before (a) and after bubbling a test tube with water (50 ml) with ambient air (b, c). Passing the air of the working area through the water sample (50 ml) with specific electrical conductivity 4.1 µS/cm for 10 min at a speed of 72 liters per hour led to an increase in this indicator upto 5.4 µS/cm.

According to the data of X-ray diffraction analysis, the crystals remaining on the substrate after the evaporation of free water belong to sodium chloride. SIMS data indicate air and water pollution with soot and salts of alkali and alkaline earth metals [2].

In accordance with our views, the elements of the dispersed phase (DP) are hydrophilic particles (NaCl microcrystals) surrounded by a thick layer of liquid crystalline hydration water [1-4]. DF has a viscous consistency, evaporates at a temperature of ~ 300 ° C, does not dissolve in organic solvents, and undergoes erosion in hypertonic saline solutions [4,5]; coagulates in the volume of water, forming loose aggregates.
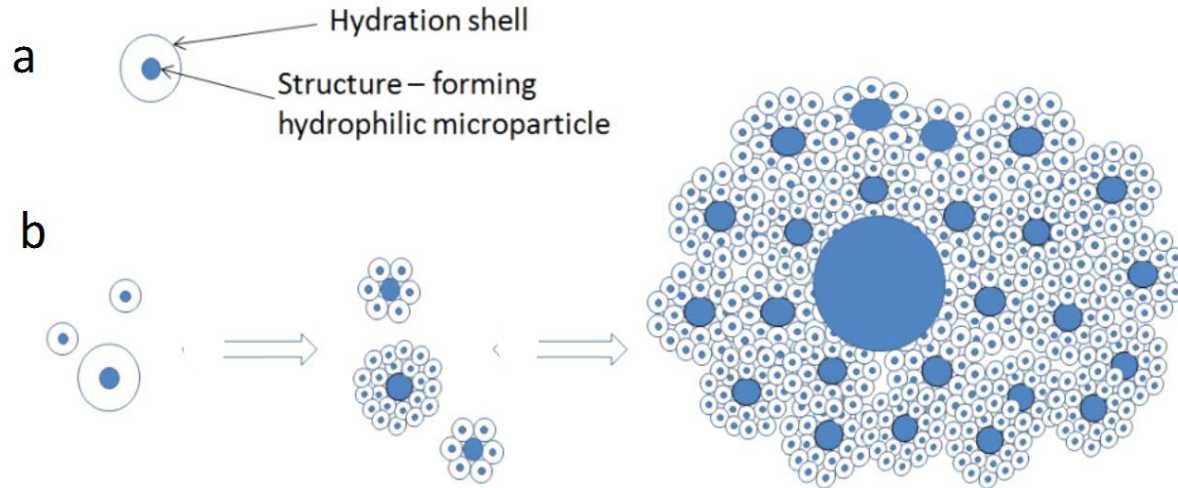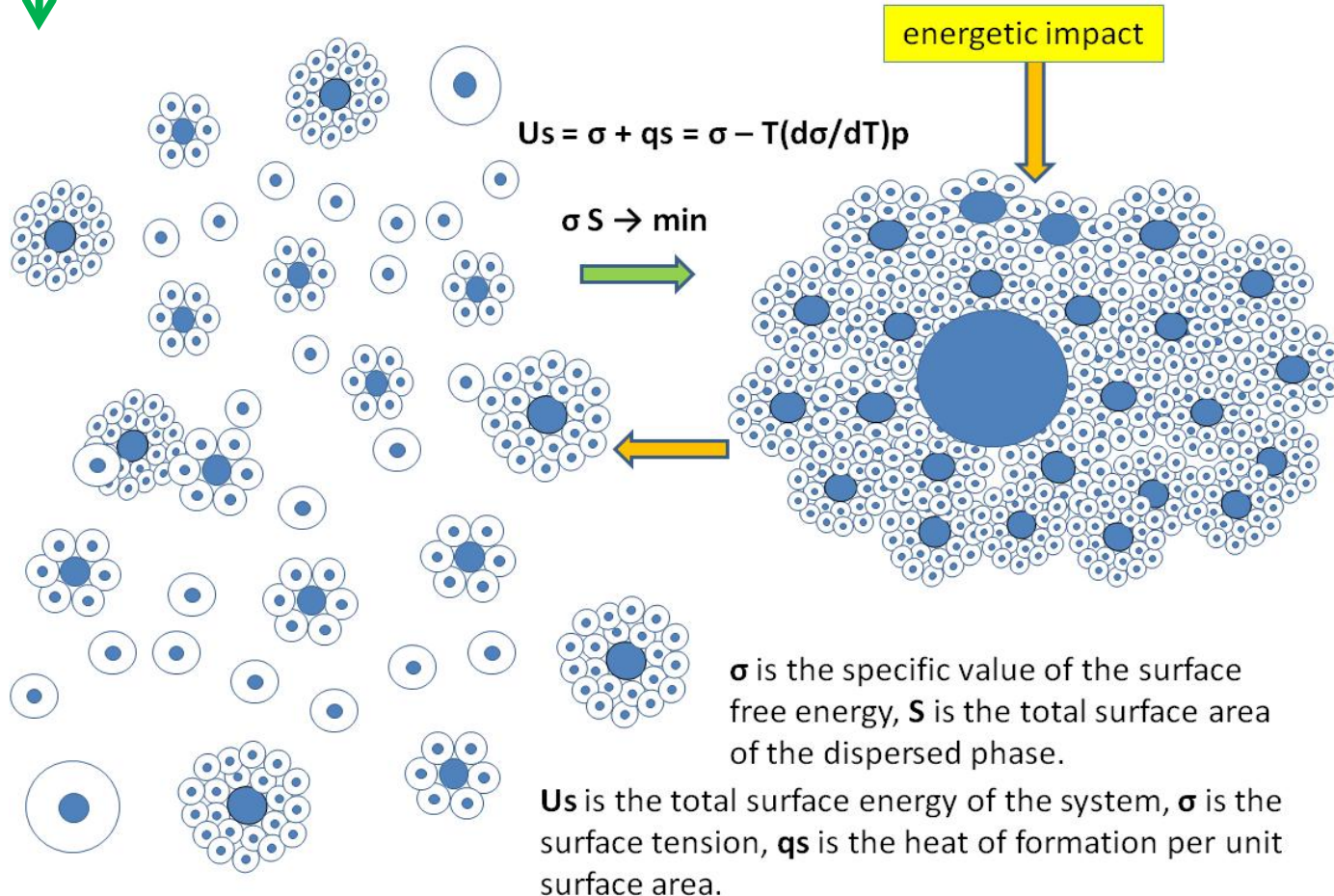

Schematic representation of the structural unit of the microdispersed phase (a) and the formation of aggregates visible through an optical microscope (b).

5. T. Yakhno, V. Yakhno. Structure and Dynamics of Aqueous Dispersions // in the Open Access book, "Colloids - Types, Preparation and Applications" edited by Prof. Mohamed Nageeb Rashed, London, UK, 2020, pp. 1-30. DOI: 10.5772/intechopen.94083. https://www.intechopen.com/chapters/73574

An increase in the dispersion of the medium is accompanied by a change in a number of its physicochemical properties.

dispersion (surface area); pH; specific electrical conductivity, ultrasound speed

electrical capacity; viscosity; surface tension; Redox potential

energetic impact

$$Us = \sigma + q_s = \sigma - T(d\sigma/dT)p$$

$$\sigma S \rightarrow min$$

σ is the specific value of the surface free energy, **S** is the total surface area of the dispersed phase.

Us is the total surface energy of the system, σ is the surface tension, **qs** is the heat of formation per unit surface area.

The direction of changes in the physicochemical parameters of water depends not on the nature of the energy impact, but on its dose
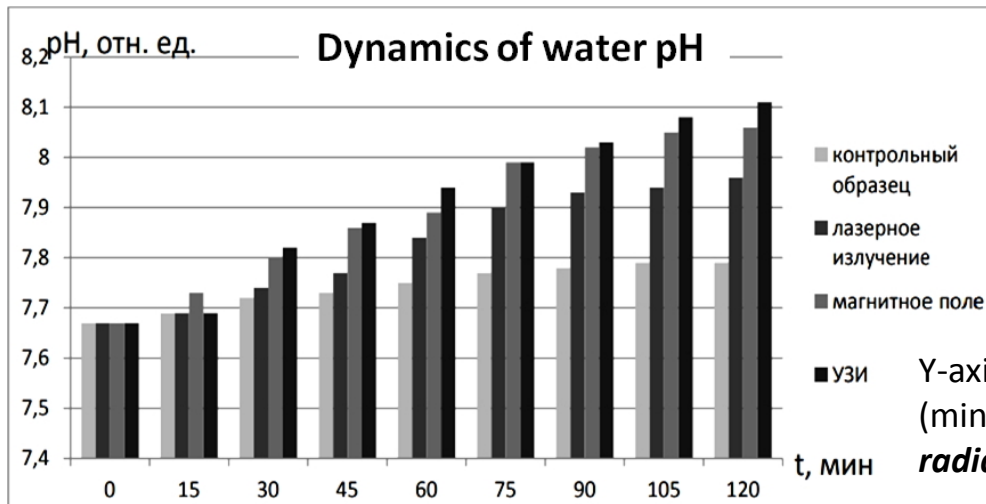
Musienko KS, Ignatova TM, Glazkova VV (2014). Studying the influence of physical fields on the physicochemical properties of water. *Biomedical Engineering and Electronics,* 2. URL: biofbe.esrae.ru/199-963. (in Russian)

Y-axis is pH (relative units); X – axis is exposure time (min). *Column order from left to right: control; laser radiation; a magnetic field; ultrasonic radiation.*
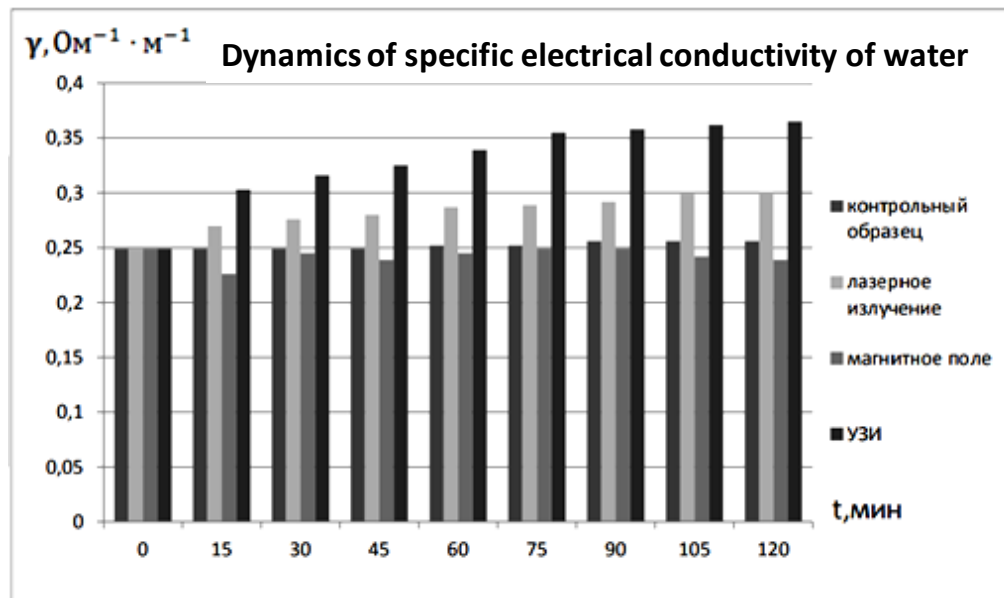

Y-axis is specific electrical conductivity; X – axis is exposure time (min). *Column order from left to right: control; laser radiation; a magnetic field; ultrasonic radiation.*

Analysis of the literature showed that external energy of any nature influences on tap, distilled, bidistilled and deionized water lead to unidirectional changes: **a decrease** in electrical capacity, viscosity, surface tension, Redox potential, **an increase** in pH and electrical conductivity, *which, in general, improves the assimilation of such water by plants and animals.*

✓**Gulyaev** Yu.V., Eremin S.M., Markov I.A., Novoselova E.G., Novikov V.V., Ten Yu.A., Fesenko E.E. Physico-chemical properties of reagent-free water and its biological activity. *Journal of Radioelectronics*, 2005, 11 (electronic journal, ISSN 1684-1719) (in Russ.)

✓**Kulagina** V.A., Sapozhnikova E.S., Stebeleva O.P., Kashkina L.V., Zheng Ch.-I., Li Ts., Lee F.-Ch. Features of the effect of cavitation on the physicochemical properties of water and effluents. Journal of Siberian Federal University. Engineering & Technologies, 2014, vol. 5, no 7, p. 605-614 (in Russ.)

✓**Chirkova** V.Yu., Stas I.E. Diagnosis of changes in physico-chemical characteristics of deionized water due to electromagnetic field effect and various methods of degasation. News of Altai State University, 2014. DOI 10.14258 / izvasu (2014) 3.1-44. (in Russ.)

✓**Anosov** A.V., Trukhan E.M. The variation of the vector potential in the laboratory changes the biological properties of water. Biophysics, 2012, vol. 57, no. 3, p. 389-394. (in Russ.)

✓**Yakhno** T.A., Uvarov V.M., Sanin A.G., Kazakov V.V. Hydro-shock-cavitation effect on water, or where do protons disappear? Materials of reports of the V Congress of Biophysicists of Russia, October 4-11, 2015, Rostov-on-Don, vol. 2, p. 339. (in Russ.)

✓**B.I. Laptev**, G.N. Sidorenko, N.P. Gorlenko, A.K. Kulchenko, Yu.S. Sarkisov, L.A. Antoshkin. Evaluation of the structure of water and aqueous solutions of sodium chloride using dielectrometry and resonance method. // Bulletin of Tomsk State University of Architecture and Building, 2013, 2, 235-244 (in Russ.)

✓etc...

Several examples from our practice

We conducted a small experiment on swirling water using the IKEA Product, milk frother. Bottled natural water "Aquanica" with a total mineralization of 200-500 mg / l was used. The pH and Redox potential were measured before and after 10 minutes of exposure to the foaming agent on water, as well as 1, 2 and 3 hours after exposure. Whipping water for ten minutes with a rotating whisk resulted in a 4% increase in pH and an 8% decrease in Redox potential The changes persisted during the observation time (3 hours). The microscopic picture of water before and after exposure is shown
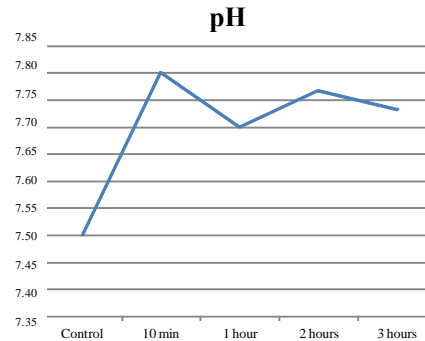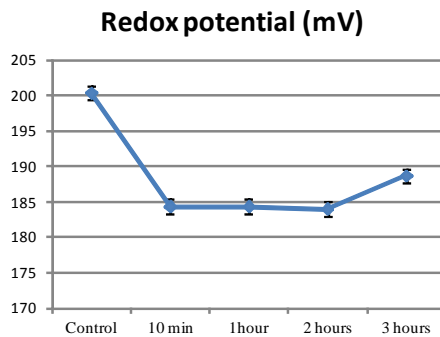
Change in Redox potential (left) and pH (right) of natural water "Aguanica" after 10 - minute operation of the foamer
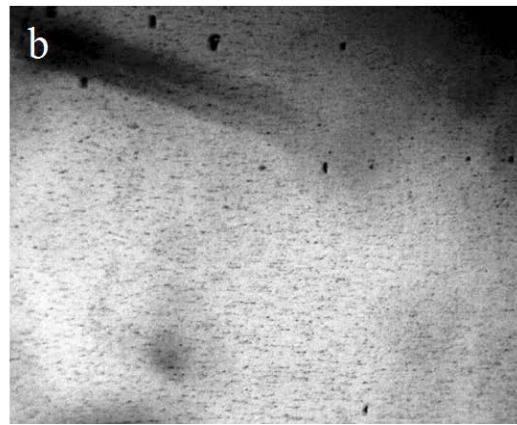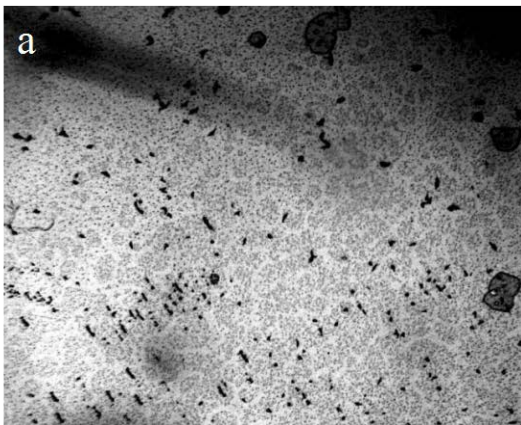

Microstructure of mineral water "Aquanika" in a thin layer (~ 8 microns) between the slide and the cover glass: a - control; b - 2 hours after operation of the foamer for 10 minutes. **Destruction of DP aggregates is noticeable.**
The width of each frame is 3 mm

Change in the capacitive conductivity of a cell with mineral water at a frequency of 60 kHz for 1.5 hours before (a) and after (b) irradiation (10 min) with green light (20 mW).

Осциллограмма изменений емкости ячейки с водой
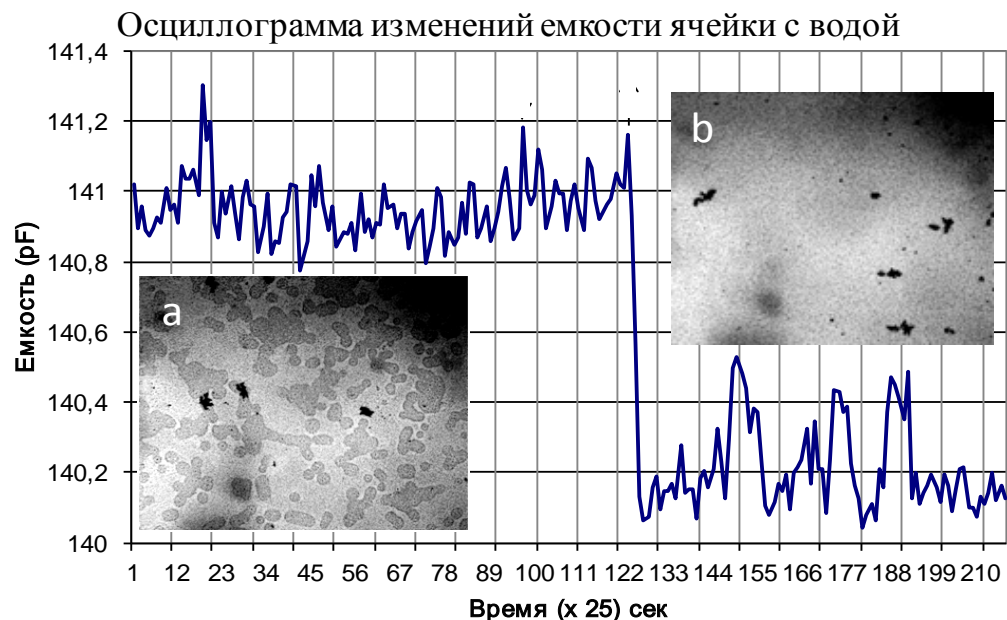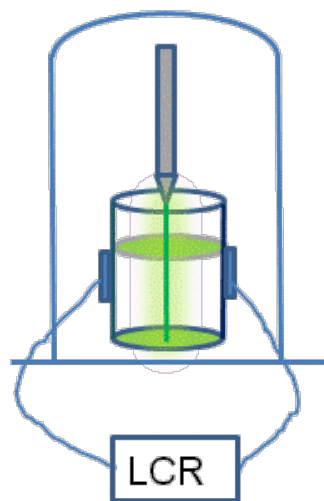
Low-intensity light also leads to the dissociation of the microdispersed phase of water. Figure shows the result of irradiating water with a 20 mW green LED laser for 10 minutes. Natural mineral drinking water "Serafimov Dar" was used in the experiment. Water was poured into a 100 ml glass beaker; the light source was placed vertically directly above the water surface in the central zone equidistant from the glass walls. In this case, a decrease in the electrical capacity of the liquid by ~ 1 pF was also noted. The microdispersed phase of water was examined under a microscope before (a) and after (b) irradiation. **Destruction of DP aggregates is noticeable**.

Yakhno TA, Pakhomov AM, Sanin AG, Yakhno VG (2018). The effect of low-intensity light on the structural and dynamic parameters of water. Proceedings of the VIII International Congress "Weak and Superweak Fields and Radiations in Biology and Medicine", 2018, St. Petersburg, 8, 99. (in Russian).

We made sure that each impact on water is accompanied by the destruction of DP aggregates and an increase in the interfacial area. **Let us trace how the dispersion of the system affects its other thermodynamic parameters.**

"Preliminary consideration shows that dispersion is an independent and full-fledged thermodynamic parameter of the system. … Thus, the surface tension is a partial derivative of any thermodynamic potential with respect to the interfacial area at constant corresponding parameters" (**L.P. Borilo**. *Thin-film inorganic nanosystems (ed. prof. Kozik VV). - Tomsk: Tomsk State University, 2012, 134 p. ISBN 978-5-94621-362-2 (In Russ.).*

The factor of the surface energy intensity is the surface tension caused by the uncompensated field of intermolecular forces at the interface. For a heterogeneous system, relative to the change in the internal energy U_r, can be written as:

$$dU = -TdS - pdV + \sigma ds + \Sigma \mu_i dn_i + \varphi dq.$$

If S, V, n_i and q are constant, then

$$\sigma = \left(\frac{\partial U}{\partial s} \right)_{S,V,n_i,q},$$

that is, **surface tension is a partial derivative of the internal energy with respect to the area of the interface at constant entropy, volume, number of moles of components and charge**. The latter can be written with respect to other thermodynamic potentials, namely the Gibbs energy G, the Helmholtz energy F and the enthalpy H, then with the corresponding constant parameters we get:

$$\sigma = \left(\frac{\partial U}{\partial s} \right)_{S,V,n_i} = \left(\frac{\partial H}{\partial s} \right)_{S,p,n_i} = \left(\frac{\partial F}{\partial s} \right)_{T,V,n_i} = \left(\frac{\partial G}{\partial s} \right)_{T,p,n_i}$$

Noteworthy is the fact that *the thermodynamic determination of the surface tension is similar to the determination of the chemical potential, only the surface tension characterizes the interfacial surface, and the chemical potential characterizes the solute. Both quantities are partial derivatives of any thermodynamic potential, but in one case - by the surface area, in the other - by the number of moles of the substance.*

"It is convenient to classify surface phenomena in accordance with the combined equation of the first and second principles of thermodynamics. For a dispersed system, it can be written in the following form:

$$dG = -SdT + Vdp + \sigma ds + \Sigma\mu_i dn_i + \varphi dq,$$

where G is the Gibbs energy; S – entropy; T is the temperature; V - volume; p — pressure; σ-surface tension; s — surface area; μ_i – chemical potential of component i; n_i is the number of moles of component i; φ – electric potential; q is the amount of electricity." **(L.P. Borilo, 2012**).

Thus, literature data and our own experiments lead to the conclusion that "water activation" occurs not at the molecular, but at the microlevel, regardless of the nature of the disturbing factor, and is associated with the downsizing of DP aggregates - an increase in the interfacial area.

[The energy of coagulation bonds is ~ $10^{-18} – 10^{-19}$ J (N. B. Uriev, 1998)].

Water phases at room conditions

More than 70 years ago (see the review *by J.C. Henniker - The depth of surface zone of a liquid. RMP, 21 2, 322-341),* convincing experimental facts were obtained indicating that water near hydrophilic surfaces forms a new phase - a near-surface layer, which differs greatly in terms of its physical properties from bulk water. The thickness of this layer is up to hundreds of microns. Direct evidence was presented for the existence of a new aqueous phase, including taking into account the refractive index, diffraction of X-ray and neutron radiation, viscosity, adhesion, and the presence of long-range order in structural ordering. The molecular weight of polywater (water-II, according to Deryagin) determined from the vapor density exceeded this indicator for ordinary water by 8-10 times, and the absorption in the IR region was characterized by two peaks that are not characteristic of any other known substance (Lippincott ER, Stromberg RR, Grant WH, Cessac GL Polywater. // Science, 1969, 164, 1482–1487). Based on the data obtained, it was assumed that the new substance is a polymer consisting of water molecules combined into hexagonal cells.

The absorption in the IR region was characterized by two peaks that are not characteristic of any other known substance **- 1595 см-1** and doublet **in 1400-1** (Lippincott et al, 1969)

a

Charge -8

b

o – oxygen
● - hydrogen

Lippincott et al, 1969
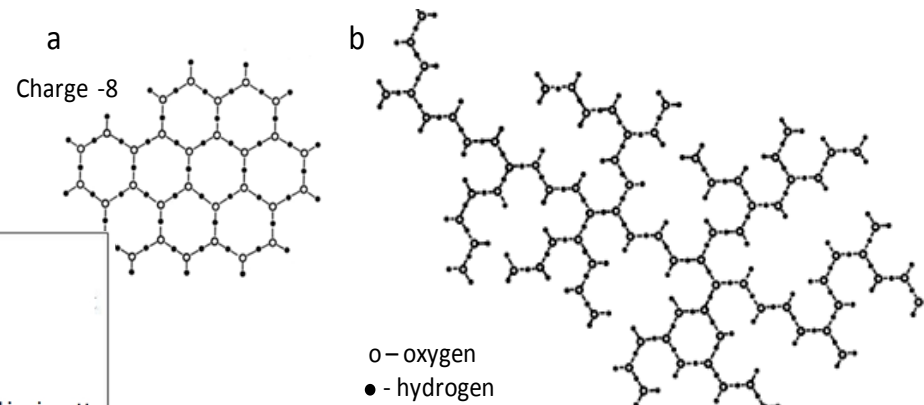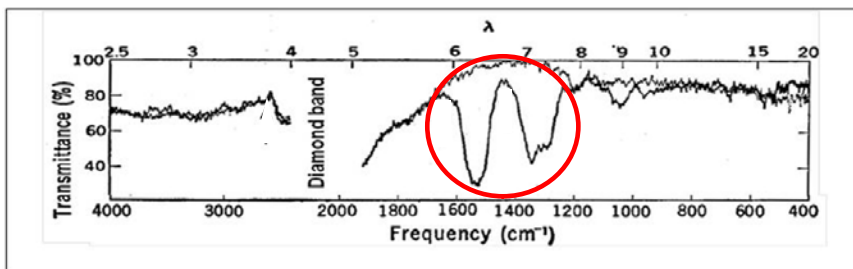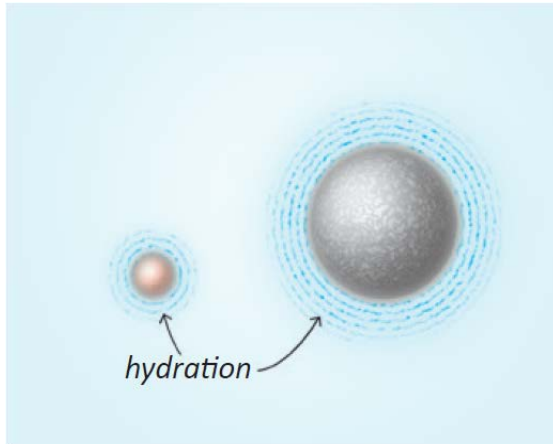
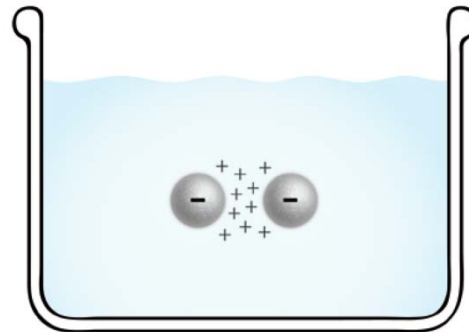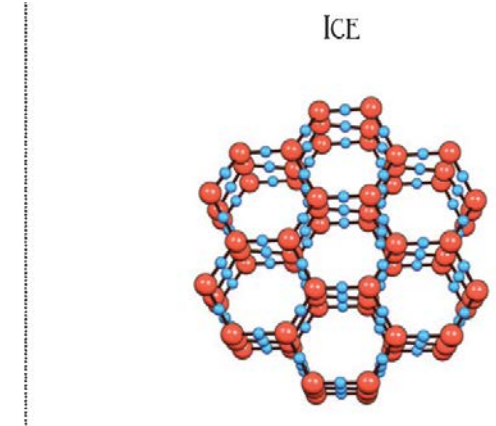# G. Pollack. The fourth phase of water, 2013


Fig. 8.13 *Similar hydration of molecule and particle implies that dissolution and suspension are similar in principle.*

HONEYCOMB SHEET
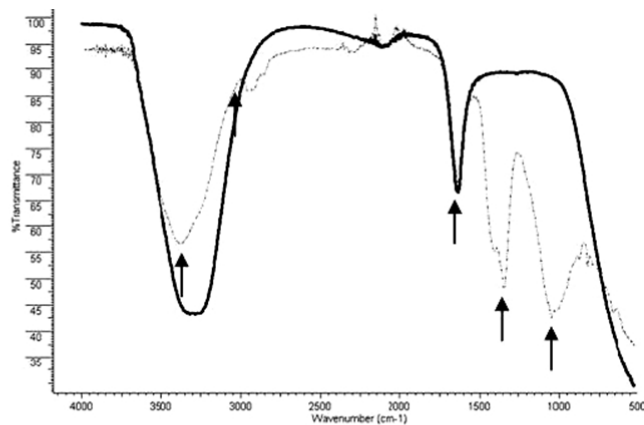
oxygen
hydrogen
EZ layers
material

ICE

The viscoplastic properties of hydration shells are determined by the weak (electrostatic) forces of vertical attachment of the hexagonal layers.

According to Ostroverkhov, the hydrogen network of interfacial water (EZ) consists of ordered (ice) and disordered (liquid) structures (**Ostroverkhov et al., 2005**). Since ions cannot be repelled by a disordered structure, the degree of ion rejection cannot reach 100%. Even in the case of ice, ions can be trapped inside ice crystals at high salt concentrations (Rubinsky, 1983; Vrbka and Jungwirth, 2005). Consequently, EZ contains a mixture of ordered and disordered structured water and a certain amount of chloride ions, but in concentrations lower than their concentration in the bulk of the solution. See also: **Zhang Y, Takizawa S, and Lohwacharin J.** Spontaneous particle separation and salt rejection by hydrophilic membranes. // WATER 2015, 7, 1-18). At the same time, the concentration of ions and particles in free water increases, also **increasing its osmotic pressure [Chaplin, 2012; Yakhno and Yakhno, 2017].**

The authors of the discovery of "polywater" (Derjagin et al) also obtained it by contacting ordinary water with hydrophilic surfaces - **fused quartz and glass**. According to Lo et al (2009), the structures they discovered - **stable water clusters at room temperature** - also had characteristic differences in the IR spectrum from ordinary water: the absorption peaks for pure water are 3283.5 cm-1 and 1634.5 cm- 1. The absorption peaks **for stable water clusters are 3371.4 cm-1, 1639.5 cm-1, 1342 cm-1, 822.5 cm-1. We see the same "red shift" and characteristic absorption for "water structures", obtained by other authors by iteratively contacting a number of hydrophilic surfaces with water.** (see the next Table).
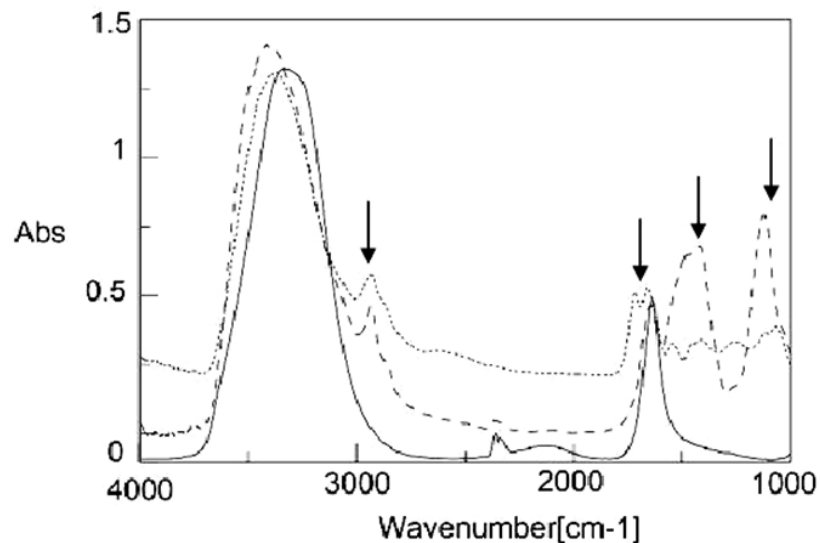
IR spectra residue of INW (dotted line) and liquid water (black line) at room temperature. The main differences are the overall red-shift of the broad OH stretching peak and the appearance of an absorption line at about 2926 cm^{-1}.

Elia et al, 2013

Elia V, Ausanio G, De Ninno A, Gentile F, Germano R, Napoli E, Niccoli M (2013). Experimental evidence of stable aggregates of water at room temperature and normal pressure after iterative contact with a Nafion® polymer membrane. WATER, 5, 16–26. doi: 10.14294/WATER.2013.4.


Infrared spectra for pure water (solid line) and solid sample of stable-water-clusters (broken line). The absorption peaks for pure water are 3283.5 cm^{-1} and 1634.5 cm^{-1}. The absorption peaks for stable-water-clusters are 3371.4 cm^{-1}, 1639.5 cm^{-1}, 1342 cm^{-1}, 822.5 cm^{-1}.

Lo et al, 2009

Lo S.Y, Geng X, Gann D (2009). Evidence for the existence of stable-water-clusters at room temperature and normal pressure. *Phys. Lett. A*, **373**, 3872–3876. doi:10.1016/j.physleta.2009.08.061.
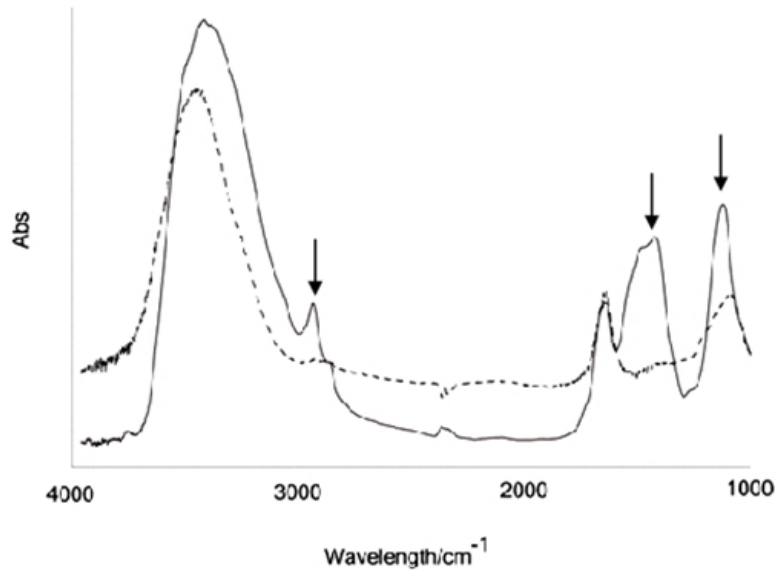
IR spectrum of lyophilized Iterative Filtration Water (IFW) sample (black line). The broken line is the spectrum obtained preparing the pellet with milli-Q water (see text).

Elia V, Ausanio G, De Ninno A, Germano R, Napoli E and Niccoli M (2013). Experimental Evidences of Stable Water Nanostructures at Standard Pressure and Temperature Obtained by Iterative Filtration. WATER, doi: 10.14294/WATER.2013.11.
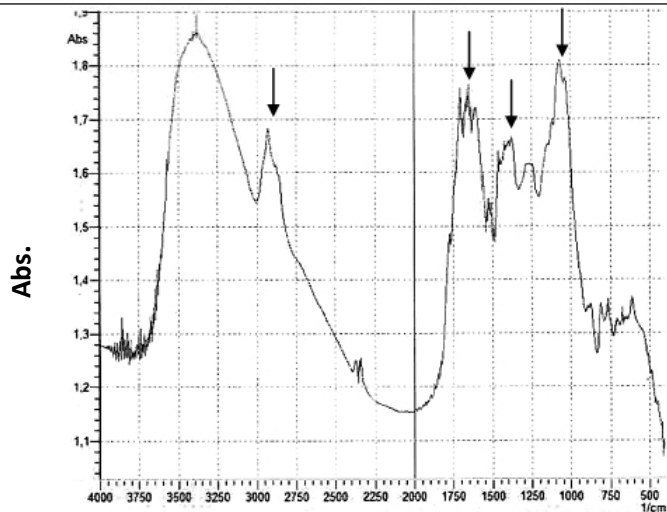
Along with residues of free water (3381.2 cm-1), there are bands characteristic of structured water (2926 cm^{-1}; ~ 1600 cm-1, ~ 1400 cm-1, ~ 1100 cm-1).

Yakhno et al, 2017

Yakhno TA, Yakhno VG, Zanozina VF (2017). Phase transitions of water as a source of slow oscillatory processes in liquid media. Proceedings of the XII International Science-Technical Conference "Modern Trends in Biological Physics and Chemisitry", Sevastopol, Russia, 2–6 October 2017; 23–27. (In Russ.).

Yinnon et al, 2016. Water Ordering Induced by Interfaces: An Experimental and Theoretical Study
doi: 10.14294/WATER.2015.3

Line	Properties of EZ water	→ Inference	Properties of INW	→ Inference
1	Ultraviolet -visible electromagnetic radiation (UV-vis) absorption, with maximum at ~270 nm. For example, at distances larger than 400 µm from Nafion, UV-vis spectra are flat and the same as for ordinary bulk water, but at smaller distances a broad peak with center at ~270 nm appears.[3]	Electronic wave-function of EZ water differs from that of bulk water.[33-35]	UV-vis absorption, with broad maximum at ~270 nm.[24]	Nafionization process affects electronic wave-function of water.
2	IR absorption of EZ water differs from that of bulk water. IR radiation emission is much lower for EZ water than for its adjacent bulk water. Differences are not due to heat gradients.[3,13]	Inter- and intra-molecular coupling in EZ water differs from that of bulk water.[33-35]	Solid residue of lyophilized INW has a red shifted H_2O main stretching band.[25] Also at ~ 2926 cm^{-1}, 1418 cm^{-1} and 1105 cm^{-1} peaks appear, which are absent in bulk water's IR spectrum.[25] Deconvolution of the residue's OH stretching peak between 2880 and 3800 cm^{-1} reveals the component at ~3600 cm^{-1} present in bulk water is absent in the residue, just as it is absent in ice – I_h.[25] The solid residue shows an excellent thermal stability (see TGA).	The structure of the residue of lyophilized INW resembles that one of ice.[25]
3	pH altered by immersing a hydrophilic or reactive metal sheet in water,[9,13,14] e.g., on immersing a Nafion sheet, pH at a distance of 1 cm from the membrane decreases from 7 to ~ 5.5, while at the EZ - bulk water boundary pH ≈ 3 .	H_2O dissociation affected by interfaces.[9,13]	pH of INW is much lower than pH of Milli-Q water.[24-26] For some samples, the pH of INW reaches values as low as 3.	pH of INW values are not due to impurities released by Nafion.[25-26]

Table continuation

4	Viscosity of EZ water is about ten-fold higher than the viscosity of bulk water.[3]	Ordering of molecules in EZ water is higher than in bulk water.	Viscosity of INW's H_2O aggregates is higher than the viscosity of bulk water.[25]	Aggregates' molecular ordering is higher than that one of bulk water.
5	EZ water is observable ~30 s after insertion of a hydrophilic or reactive metal sheet. Sheet type determines: (a) EZ expansion rate -- few µm/s; (b) time required for reaching maximum width and stabilization ~ one day.[3]	Molecular ordering takes place over a macroscopic time scale.[3]	H_2O ordering induced by repetitive immersions of the Nafion membrane in water, after agitations are halted and the membrane is removed, persist. At least for 90 days the remnant liquid has properties differing from those of bulk water.[24,25]	Molecular ordering takes place and persists over a macroscopic time scale.[24-26]
6	EZ water's width is of the order of 10^{-5}-10^{-4} m.[3]		H_2O aggregates' diameter is of the order of 10^{-5} m.[25]	

*Superscripts numbers refer to reference in which findings were observed or analyzed.

This analyses show **that INW's H2O aggregates have numerous characteristics similar to those of exclusion zone (EZ) water**, i.e., the zone adjacent to hydrophilic membranes like Nafion or to reactive metals.

Table 2 Similarities and dissimilarities between IPW-CE, IPW-HC and IPW-N

Property	Property is true for IPW-CE	Property is true for IPW-HC	Property is true for IPW-N	Simila
Contains 10^{-4} m sized associates	Yes	Yes	Yes	Yes
Concentration of associates	$\sim 10^{-4}$ mol L^{-1}	$\sim 10^{-3}$ mol L^{-1}	$\sim 10^{-4}$ mol L^{-1}	No
UV absorbance typical of structured water	Yes	Yes	Yes	Yes
Broad UV emission band typical of excimers around 350 nm	Yes	Yes	Yes	Yes
Broad UV emission band typical of excimers around 440 nm	Yes	Yes	No	No
Optical activity typical of β-sheets	Yes	Yes	Yes	Yes
Optical activity resistant to prolonged heating	Yes	Yes	No	No
Fractally structured	Yes	Yes	Yes	Yes
Electric conductivity higher than Milli-Q® water	Yes	Yes	Yes	Yes
Density higher than that of Milli-Q® water	Yes	Yes	Yes	Yes
Linear correlation between χ_{IPW} and other physicochemical variables	Yes	Yes	Yes	Yes
Properties of linear correlation are perturbing membrane specific	Yes	Yes	Yes	Yes
Sign of the dependence of the pH on χ	Positive—liquid is alkaline	Positive—liquid is alkaline	Negative—liquid is acidic	No
Contains solely H$_2$O	No	Yes	Yes	No
Contains organic polymers	Yes	No	No	No

The following variables are altered by perturbing water with cellulose polymers: pH; electric conductivity; heat of mixing with acids or bases; density; and spectra, i.e., its ultraviolet (UV) and visible (vis) light absorption and fuorescence spectra, and its infrared spectra; images obtained with atomic force microscopy, fuorescence microscopy or optical microscopy

Thus, all the detected stable water structures have similarities in the features of the IR spectrum, characteristic of polywater. This means that there are only two phases of water - continuous and near-wall (EZ), and the latter can also exist in the form of "water structures": EZ near hydrophilic impurities [Yakhno and Yakhno (2019)] or EZ exfoliating from the substrate [Zhang et al (2015)].

"Apparently, we are first to report that high refractive indices of water-containing objects are connected with the structured water component... Some gels and biological objects with large (up to 95-99%) proportion of water have a refractive index (RI) (n = 1,42-1,50), significantly higher than RI (n_0 = 1,333) of ordinary water. A natural question arises: is the high value of RI an attribute of structured water? We here show that analysis of published data allow us to give a positive answer to this question. ...
We assume that, similarly to the above example, water can only be in two states: bulk and structured. " [V. Tychinsky. High electric susceptibility is the signature of structured water in water-containing objects. // doi: 10.14294/WATER.2011.8].

We believe, that this second phase of water has a single structure and corresponds to the previously described polywater [Lippincott et al (1969)].

Thank you for your attention!

Good luck in job!