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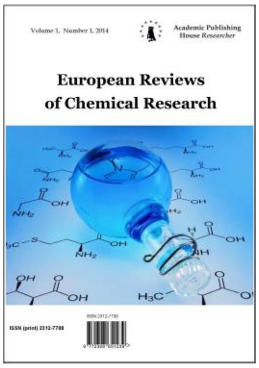

Articles and Statements

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Hydrochemical Deposition of Cu_2S Films Using Thiocarbamide

[1] Irina A. Glukhova
[2] Larisa N. Maskaeva
[3] Vyatcheslav F. Markov
[4] Stanislav S. Tulenin
[5] Anna I. Shemyakina

[1] Ural Federal University named after the first President of Russia B.N. Yeltsin, Russian Federation
620002 Ekaterinburg, Mira Str., 19
E-mail: anutan145@mail.ru
[2] Ural Federal University named after the first President of Russia B.N. Yeltsin, Russian Federation
620002 Ekaterinburg, Mira Str., 19
D. Sc. (Chemical), Professor
E-mail: mln@ural.ru
[3] Ural Federal University named after the first President of Russia B.N. Yeltsin, Russian Federation
620002 Ekaterinburg, Mira Str., 19
D. Sc. (Chemical), Professor, head of the department of physical and colloidal chemistry.
E-mail: v.f.markov@ustu.ru
[4] Ural Federal University named after the first President of Russia B.N. Yeltsin, Ekaterinburg, Russian Federation
620002 Ekaterinburg, Mira Str., 19
E-mail: stast1989@mail.ru
[5] Ural Federal University named after the first President of Russia B.N. Yeltsin, Russian Federation
620002 Ekaterinburg, Mira Str., 19
E-mail: anutan145@mail.ru

Abstract

Hydrochemical deposition of the films of stoichiometric composition Cu_2S was determined in ammoniac and acetated layer systems by energy-dispersive elemental analysis. The film composition almost corresponds to formula unit Cu_2S. Electron-microscopic research of the film morphology showed that the particles, which are formed the films of Cu_2S have average size ~10 nm.

The authors conclude that:

1. Nanocrystal films of copper (I) sulfide with the thickness 100±10 nm exhibiting good adhesion to sitall substrate were obtained by hydrochemical deposition in systems «$CuSO_4$ – NaAc – $CS(NH_2)_2$» and «$CuSO_4$ – NH_3 – $CS(NH_2)_2$». EDX analysis confirmed that at hydrochemical deposition the formation of thin Cu_2S film phase which is closed to stoichiometric composition

with the average content of metal and sulfur 66.59 and 33.41 at.%, 66.82 and 33.18 at.% in acetated and ammoniac systems correspondingly occurs.

2. Morphology of obtained films Cu_2S was studied by electron-microscopic research, their nanocrystal nature was determined.

Keywords: hydrochemical deposition, thin films, copper (I) sulfide, surface morphology, raster electron microscopy.

Introduction

Different methods of production of copper (I) sulfide layers are known: solid phase reaction [1], pyrolysis [2, 3], sputtering [4], photochemical method [5, 6], chemical deposition from aqueous solutions [7, 8], vacuum vaporization [9]. Method of synthesis has a significant influence on the variety of film phase states: from Cu_2S to CuS_2 [10], and therefore – on the structure and morphology of their surface.

As it was shown in our previous paper [11] the advantage of copper (I) sulfide hydrochemical deposition is that it allows to control the changes of the fraction of free metal ions in the reaction mixture by using ligands with different strengths for copper. The control of both copper complex degrees in the solution and process temperature gives an opportunity to vary the characteristics of growing films of $Cu_{2-x}S$: elemental composition, microstructure, and size of particles, their electrical and optical properties.

It is known that hydrochemical deposition of metal sulfide layers is based on interaction of metal salts in alkaline with chalcogenizer that is usually thiocarbamide or its compounds [12]. Earlier chemical deposition of Cu_2S from aqueous solutions by thiocarbamide $CS(NH_2)_2$ was described in [13-18], as well as by sodium thiosulphate $Na_2S_2O_3$ in [19, 20] in alkaline [13-17, 19] or in acid [18, 20]. $CuCl_2$ or $CuSO_4$ were used as copper (II) salt. In [18] the function of the complexing agent belonged to tartaric acid $C_4H_6O_6$. However, it should be mentioned that the common ligands for copper ions used by scientists are ammonia NH_3 and triethanolamine $C_6H_{15}NO_3$ [13-17, 19]. In [11] we showed that the use of complexing agents with different strengths and denticity has a great influence on deposition process rate and morphology features of thin zinc sulfide films formation.

Taking into account the information mentioned above the present article is about elemental composition and morphology of hydrochemically deposited copper sulfide films.

Experimental

Synthesis of copper sulfide films by hydrochemical deposition was made using two compound variants containing copper sulphate $CdSO_4$ as the metal source, and thiocarbamide $CS(NH_2)_2$ as the chalcogenizer. To slow down the rate of sulfide formation ammonia NH_3 was introduced (ammoniac reaction system) in one case and sodium acetate was introduced (acetated reaction system) in another case. The synthesis of copper sulfide layers in ammoniac mixture was carried out at temperature 298 K in the course of 120 min, in acetated mixture – at 343 K in the course of 45 min. Previously defatted ST-50 sitall sheets were used as substrates.

Film thickness was measured with *Linnik MII-4M interferometer*.

Surface morphology and elemental composition study of films were examined with *Scanning Electron Microscope JEOL JSM-5900LV* by Raster (Scanning) Electron Microscopy (REM) with an EDX attachment for X-Ray Spectral Electron Microprobe Analysis.

Results and discussions

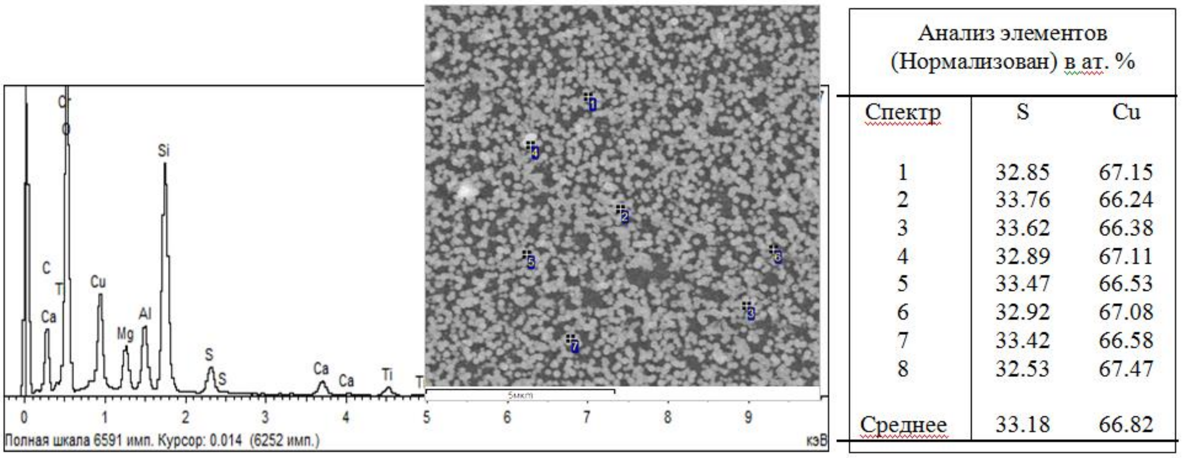
It is believed that during mixture interaction of copper sulphate $CuSO_4$ solution and complexing agents *L* (NH_3, Ac^-) with thiocarbamide the following reaction of the formation of CuS occurs:

$$CuL_x^{2+} + CS(NH_2)_2 + 4OH^- = CuS\downarrow + xL + CN_2^{2-} + 4H_2O$$

It should be noted that in the system it is possible either complete or incomplete reduction of Cu (II) to monovalent state by thiocarbamide having rather high reduction potential (-0.42V) [21, 22].

The result of hydrochemical deposition in both systems was copper sulfide films with thickness 100-110 nm with homogeneous covering of the substrate surface. Copper is in a monovalent state in them.

Figures 1-2 show electronic microscopic images of obtained films with the indication of ranges of local element analysis. Its results showed that the separate granules and interphase surface of films from ammoniac system consist of copper and sulfur with the content 66.59±and 33.41±1.0 at.%.



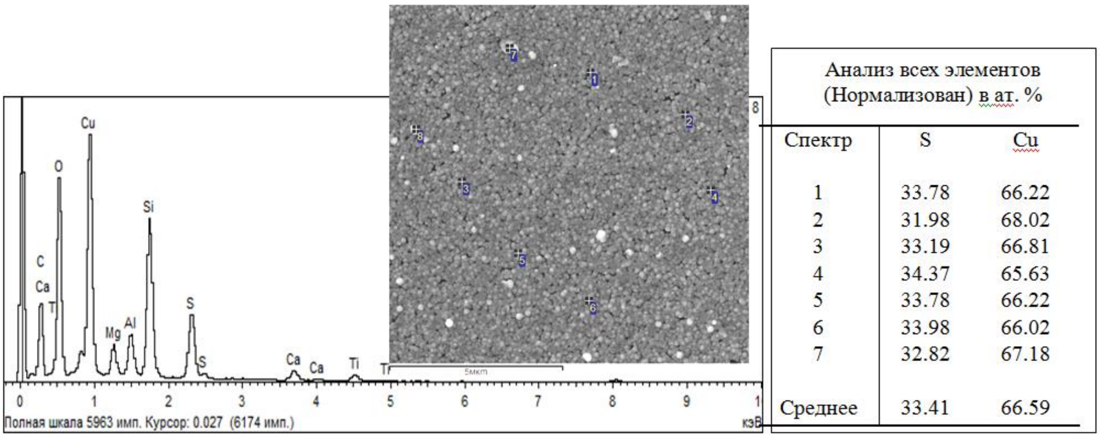
Анализ элементов (Нормализован) в ат. %

Спектр	S	Cu
1	32.85	67.15
2	33.76	66.24
3	33.62	66.38
4	32.89	67.11
5	33.47	66.53
6	32.92	67.08
7	33.42	66.58
8	32.53	67.47
Среднее	33.18	66.82

Fig. 1. Results of energy-dispersive analysis of Cu_2S film produced by hydrochemical depositin from acetated system at temperature 298 K

For layers from the acetated system these values are 66.82±0.58 and 33.18±0.58 at.% correspondingly. The obtained results show high stoichiometry of synthesized semiconductive layer of Cu_2S in both reaction systems. The presence of bands of oxygen, calcium, titanium, magnesium, aluminium, silicon is determined by the nature of sitall substrate consisting of oxides of elements mentioned above.

It should be noted that more homogeneous composition of copper (I) sulfide film was obtained from acetated reaction bath.



Анализ всех элементов (Нормализован) в ат. %

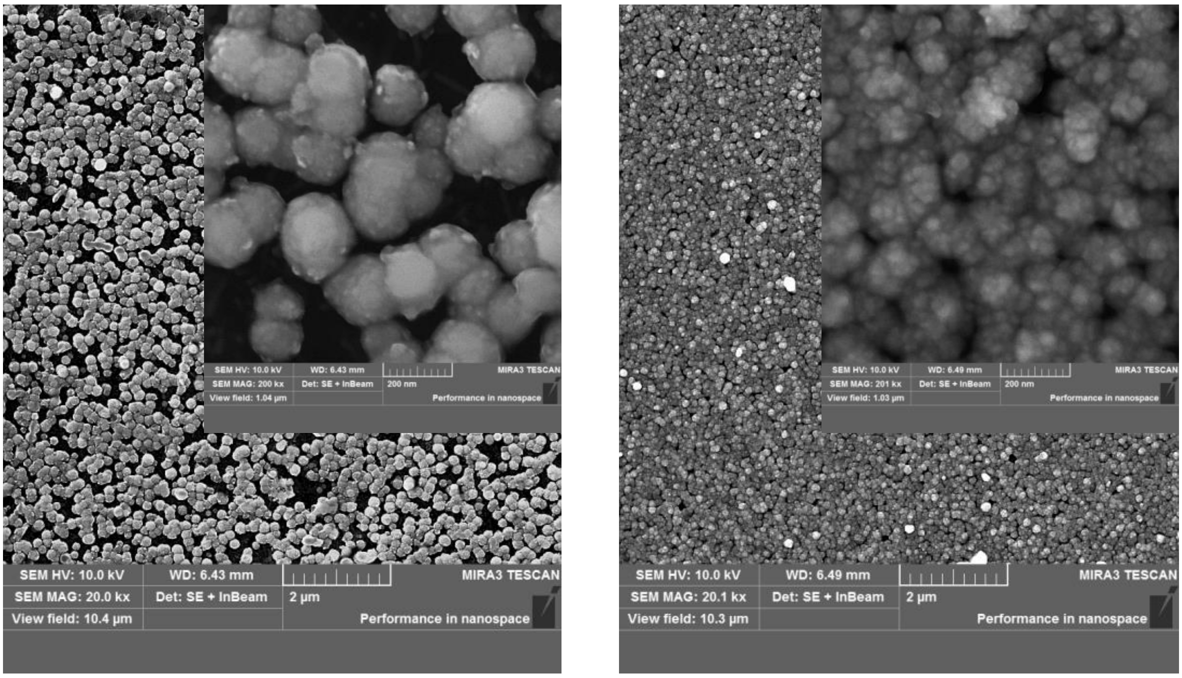
Спектр	S	Cu
1	33.78	66.22
2	31.98	68.02
3	33.19	66.81
4	34.37	65.63
5	33.78	66.22
6	33.98	66.02
7	32.82	67.18
Среднее	33.41	66.59

Fig. 2. Results of energy-dispersive analysis of Cu_2S film produced by hydrochemical depositin from ammoniac system at temperature 343 K

To study the surface relief of Cu_2S films synthesized in ammoniac and acetated reaction systems raster electron microscopy method was used. Microimages are given on Fig. 3.

Microimages show that the most homogeneous layer of copper sulfide is formed on the sitall matrix surface from acetated system. It has a rather dense arrangemnet. Layers from ammoniac reaction system are distinguished by lower uniformity. It can be explained by the following.

The calculated values of supersaturation show that the formation of copper sulfide film in both systems ammoniac (1.59×10^{10}) and acetated (1.52×10^{8}) occurs in high supersaturated solutions. However, it should be considered that the calculation of ionic equilibria was made at 298 K for both systems; whereas hydrochemical synthesis of copper sulfide films in acetated bath was carried out at 343 K. Temperature increasing intensifies synthesis process, increasing the rate of interaction between copper and thiocarbamide with the formation of sulfide solid phase.



а *б*

Fig. 3. Electron-microscopic images of Cu_2S films deposited at 298 K in the course of 120 min from ammoniac system (*а*) and at 343 K in the course of 45 min from acetated system (*б*)

Despite the significant differences in morphology of the layers obtained from studied systems it can be said that independently from the compound of baths spherical globules are the main structure elements that the layers of Cu_2S are consisted of. These globules are formations of smaller particles preliminarily of spherical shape. Undoubtedly, the size and the shape of structure elements of the film are influenced by deposition process intensity, which is determined by the conditions in reactor, particularly by different temperatures of deposition process. Thus, in acetated system (Fig.3) the formation of copper (I) sulfide film occurs from globules with enough homogeneous size (~10 nm) which attach to each other densely, forming agglomerates with the size up to 80-150 nm. In ammoniac bath where the synthesis was carried out at 298 K larger agglomerates of spherical shape with diameter 180-200 nm are formed.

Electron-microscopic images of Cu_2S films generally confirmed the signified cluster-cluster mechanism of film growth that was proved by us in research works [23, 24]. It suggests the formation of nuclei of primary clusters of solid phase in the bulk of solution, their growth and subsequent adsorption on the substrate.

One more factor that leads to differences in morphology of deposited layers of Cu_2S can be the nature influence, particularly structure-spatial parameters of ligands introduced in the system. Thus, ligands possessing branched spatial structure can make difficult the interaction of primary clusters of sulfide phase with growing Cu_2S film. First, it refers to acetate ions that have two carbon atoms, the first one is connected with three hydrogen atoms, and the second one with two oxygen atoms. Such spatial configuration makes additional difficulties for collisions of primary clusters between each other in the bulk of reaction mixture, with film surface and slows down the rate of film growth. As a result, Cu_2S layers are produced with more organized and denser surface structure. Ammonium molecule with one central nitrogen atom surrounded by three hydrogen atoms cannot have such a strong blocking influence on aggregation of particles.

Conclusion

1. Nanocrystal films of copper (I) sulfide with the thickness 100±10 nm exhibiting good adhesion to sitall substrate were obtained by hydrochemical deposition in systems «$CuSO_4$ – NaAc – $CS(NH_2)_2$» and «$CuSO_4$ – NH_3 – $CS(NH_2)_2$». EDX analysis confirmed that at hydrochemical deposition the formation of thin Cu_2S film phase which is closed to stoichiometric composition with the average content of metal and sulfur 66.59 and 33.41 at.%, 66.82 and 33.18 at.% in acetated and ammoniac systems correspondingly occurs.

2. Morphology of obtained films Cu_2S was studied by electron-microscopic research, their nanocrystal nature was determined.

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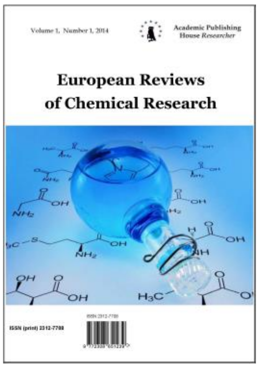

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The Reactions of Condensation–Dehydration Occurring in Aqueous Alkaline Solutions at Ph = 9–11 and T = 65–95 °C in the Process of Modeling of Primary Hydrosphere

[1] Ignat Ignatov
[2] Oleg Mosin

[1] The Scientific Research Center of Medical Biophysics (SRCMB), Bulgaria
Professor, D. Sc., director of SRCMB
1111 Sofia, N. Kopernik Str., 32
E-mail: mbioph@dir.bg
[2] Moscow State University of Applied Biotechnology, Russian Federation
Senior research, PhD (Chemistry)
103316 Moscow, Talalihina ulitza, 33
E-mail: mosin-oleg@yandex.ru

Abstract

The reactions of condensation–dehydration occurring in alkaline aqueous solutions at t = 65–95 °C and pH = 9–11, resulting in synthesis from unorganic molecules the larger organic molecules as polymers and short polipeptides in the process of modeling of primary hydrosphere, were discussed, as well as the possible mechanisms of the deuterium accumulation in form of HDO in hot water. For this aim we performed experiments with hot mineral water and seawater from Bulgaria and water with varying content of deuterium using IR- and DNES-spectroscopy. As model systems were used cactus juice of *Echinopsis pachanoi* and Mediterranean jellyfish *Cotylorhiza tuberculata*. It was demonstrated that hot alkaline mineral water with temperature from +65 °C to +95 °C and the pH value from 9 to 11 is more suitable for the origination of life and living matter than other analyzed water samples. In hot mineral waters the local maximums in IR-spectra are more manifested compared to the local maximums obtained in IR-spectra of the same water at a lower temperature. The difference in the local maximums from +20 °C to +95 °C at each +5 °C according to the Student *t*-criterion makes up $p < 0,05$.

Keywords: deuterium, hydrosphere, evolution, origin of life, IR spectroscopy, DNES.

Introduction

Previous biological experiments with D_2O and structural-conformational studies with deuterated macromolecules, performed by us, enable to modeling conditions under which the first living forms of life might be evolved [1–3]. The content of deuterium in hot mineral water may be increased due to the physical chemical processes of the deuterium accumulation. It can be presumed that primary water might contain more deuterium at early stages of evolution of first living structures, and deuterium was distributed non-uniformly in the hydrosphere and atmosphere [4]. The primary reductive atmosphere of the Earth consisted basically of gas mixture

CO, H_2, N_2, NH_3, CH_4, lacked O_2–O_3 layer protecting the Earth surface from rigid short-wave solar radiation carrying huge energy capable to cause radiolysis and photolysis of water. The processes accompanying accumulation of deuterium in the hydrosphere are solar radiation, volcanic geothermal processes and electric discharges in the atmosphere. These natural processes could lead to the enrichment of the hydrosphere by deuterium in the form of HDO which evaporates more slowly then H_2O, and condenses faster. If this is true, this is a significant fact regarding thermal stability of deuterated macromolecules in the preservation of life under thermal conditions, because chemical bonds with participation of deuterium are stronger than those ones formed of hydrogen.

The natural prevalence of deuterium makes up approximately 0,015–0,020 atom%, and depends strongly on the uniformity of substance and the total amount of matter formed in the course of early Galaxy evolution [5]. The average ratio of $D/^1H$ in nature makes up approximately 1:5700. In natural waters, the deuterium is distributed irregularly: from 0,02–0,03 mol.% for river water and sea water, to 0,015 mol.% for water of Antarctic ice – the most purified from deuterium natural water containing in 1,5 times less deuterium than that of seawater. According to the international SMOW standard isotopic shifts for D and ^{18}O in sea water: $D/^1H = (155{,}76 \pm 0{,}05) \cdot 10^{-6}$ (155,76 ppm) and $^{18}O/^{16}O = (2005{,}20 \pm 0{,}45) \cdot 10^{-6}$ (2005 ppm). For SLAP standard isotopic shifts for D and ^{18}O in seawater make up $D/^1H = 89 \cdot 10^{-6}$ (89 ppm) and for a pair of $^{18}O/^{16}O = 1894 \cdot 10^{-6}$ (1894 ppm). In surface waters, the ratio $D/^1H = \sim(1{,}32–1{,}51) \cdot 10^{-4}$, while in the coastal seawater – $\sim(1{,}55–1{,}56) \cdot 10^{-4}$. The natural waters of CIS countries are characterized by negative deviations from SMOW standard to $(1{,}0–1{,}5) \cdot 10^{-5}$, in some places up to $(6{,}0–6{,}7) \cdot 10^{-5}$, but however there are also observed positive deviations at $2{,}0 \cdot 10^{-5}$.

The constant sources of deuterium are explosions of nova stars and thermonuclear processes frequently occurring inside the stars. Probably, it could explain a known fact, why the amount of deuterium is slightly increased during the global changes of climate in warming conditions. The gravitational field of the Earth is insufficiently strong for the retaining of lighter hydrogen, and our planet is gradually losing hydrogen as a result of its dissociation into interplanetary space. Hydrogen evaporates faster than heavy deuterium, which can be collected by the hydrosphere. Therefore, as a result of this natural process of fractionation of H/D isotopes throughout the process of Earth evolution there should be an accumulation of deuterium in the hydrosphere and surface waters, while in the atmosphere and in water vapour deuterium content tends to be low. Thus, on the planet there occurs a natural process of separation of H and D isotopes, playing an essential role in the maintenance of life on the planet.

The second point regards the influence of temperature on the biochemical processes in living matter. Our recent studies have shown that the most favorable for the origin of life and living matter seem to be hot alkaline mineral waters interacting with $CaCO_3$ [6, 7]. According to the law for conservation of energy the process of self-organization of primary organic forms in water solutions may be supported by thermal energy of magma, volcanic activity and solar radiation. According to J. Szostak, the accumulation of organic compounds in small isolated lakes is more possible compared to the ocean [8]. It is most likely that life originated near a hydrothermal vent: an underwater spout of hot water. Geothermal activity gives more opportunities for the origination of life. In 2009 A. Mulkidjanian and M. Galperin demonstrate that the cell cytoplasm contains potassium, zinc, manganese and phosphate ions, which are not particularly widespread in the sea aquatorium [9]. J. Trevors and G. Pollack proposed in 2005 that the first cells on the Earth assembled in a hydrogel environment [10]. Gel environments are capable of retaining water, oily hydrocarbons, solutes, and gas bubbles, and are capable of carrying out many functions, even in the absence of a membrane. Hydrocarbons are an organic compounds consisting entirely of hydrogen and carbon. The data presented in this paper show that the origination of living matter most probably occurred in hot mineral water. This may occurred in ponds and hydrothermal vents in seawater or hot mineral water. An indisputable proof of this is the presence of stromatolites fossils. They lived in warm and hot water in zones of volcanic activity, which could be heated by magma and seem to be more stable than other first sea organisms [11].

Therefore, the purpose of the research was studying the hydrological conditions of primary hydrosphere (temperature, pH, isotopic composition) for possible processes for origin of first organic forms in hot mineral water with HDO. Various samples of water from Bulgaria, as well water with varying deuterium content were studied within the frames of the research.

Material and methods

Chemicals

For preparation of water with varying content of deuterium (HDO) was used D_2O (99,9 atom.%) purchased from the Russian Research Centre "Isotope" (St. Petersburg, Russian Federation). D_2O was preliminary distilled over $KMnO_4$ with the subsequent control of isotope enrichment by ^1H-NMR-spectroscopy on a Brucker WM-250 device ("Brucker", Germany) (working frequency: 70 MHz, internal standard: Me_4Si).

Biological Objects

The objects for the study were the cactus juice of *Echinopsis pachanoi* and the Mediterranean jellyfish *Cotylorhiza tuberculata* (Chalkida, Greece, Aegean Sea).

Water Samples

The samples of water were taken from various water springs of Bulgaria:
1 – Mineral water (Rupite, Bulgaria);
2 – Seawater (Varna resort, Bulgaria);
3 – Mountain water (Teteven, Bulgaria);
5 – Deionized water (the control).
6 – Water with varrying deuterium content (HDO).

IR-Spectroscopy

IR-spectra of water samples were registered on Brucker Vertex ("Brucker", Germany) Fourier-IR spectrometer (spectral range: average IR – 370–4000 cm^{-1}; visible – 2500–8000 cm^{-1}; permission – 0.5 cm^{-1}; accuracy of wave number – 0.1 cm^{-1} on 2000 cm^{-1}) and on Thermo Nicolet Avatar 360 Fourier-transform IR (M. Chakarova).

DNES-Spectral Analysis

The research was made with the method of differential non-equilibrium spectrum (DNES). The device measures the angle of evaporation of water drops from 72 ^{o} to 0 ^{o}. As the main estimation criterion was used the average energy ($\Delta E_{H...O}$) of hydrogen O...H-bonds between H_2O molecules in water's samples. The spectra of water were measured in the range of energy of hydrogen bonds 0,08–0,1387 eV with using a specially designed computer program.

High-Frequency Coronal Electric Discharge Experiments

A device for high-frequency coronal electric discharge was used in this study, constructed by I. Ignatov and Ch. Stoyanov. The frequency of the applied saw-tooth electric voltage was 15 kHz, and the electric voltage – 15 кV. The electric discharge was obtained using a transparent firm polymer electrode on which a liquid sample of water (2–3 mm) was placed. The spectral range of the photons released upon electric discharge was from λ = 400 to λ = 490 nm and from λ = 560 to λ = 700 nm.

Results and discussion

Studying Various Water Samples on the Feasibility for Origin of Life

We have carried out the research of various samples of mineral water obtained from mineral springs and seawater from Bulgaria (Fig. 1, curves *1–5*). For this aim we employed the IR-spectrometry and DNES method relative to the control – deionized water.

For calculation of the function *f(E)* represented the energy spectrum of water, the experimental dependence between the wetting angle (θ) and the energy of hydrogen bonds (E) is established:

$$f(E) = \frac{14{,}33 f(\theta)}{[1-(1+bE)^2]^2}, \qquad (1)$$

where $b = 14{,}33\ \text{eV}^{-1}$

The relation between the wetting angle (θ) and the energy (E) of the hydrogen bonds between H_2O molecules is calculated by the formula:

$$\theta = arcos\ (-1 - 14{,}33E) \tag{2}$$

Cactus juice was also investigated by the DNES method (Fig. 1, *curve 1*). The cactus was selected as a model system because this plant contains approximately 90 % of water. The closest to the spectrum of cactus juice was the spectrum of mineral water contacting with Ca^{2+} and HCO_3^- ions (Fig. 1, *curve 2*). DNES-spectra of cactus juice and mineral water have magnitudes of local maximums (E, eV) at –0,1112; -0,1187; -0,1262; -0,1287 and –0,1387 eV. The similar local maximums in the DNES-spectrum between the cactus juice and seawater were detected at -0,1362 eV. The DNES-spectrum of the control sample of deionized water (Fig. 1, *curve 5*) was substantially different from DNES-spectra of seawater and mineral water.

Another important parameter was measured by the DNES method – the average energy ($\Delta E_{H...O}$) of hydrogen H...O-bonds among individual molecules H_2O, which makes up -0,1067±0,0011 eV. When the water temperature is changed, the average energy of hydrogen H...O-bonds alternates. This testified about the restructuring of average energies of hydrogen H...O-bonds among individual H_2O molecules with a statistically reliable increase of local maximums in DNES-spectra.

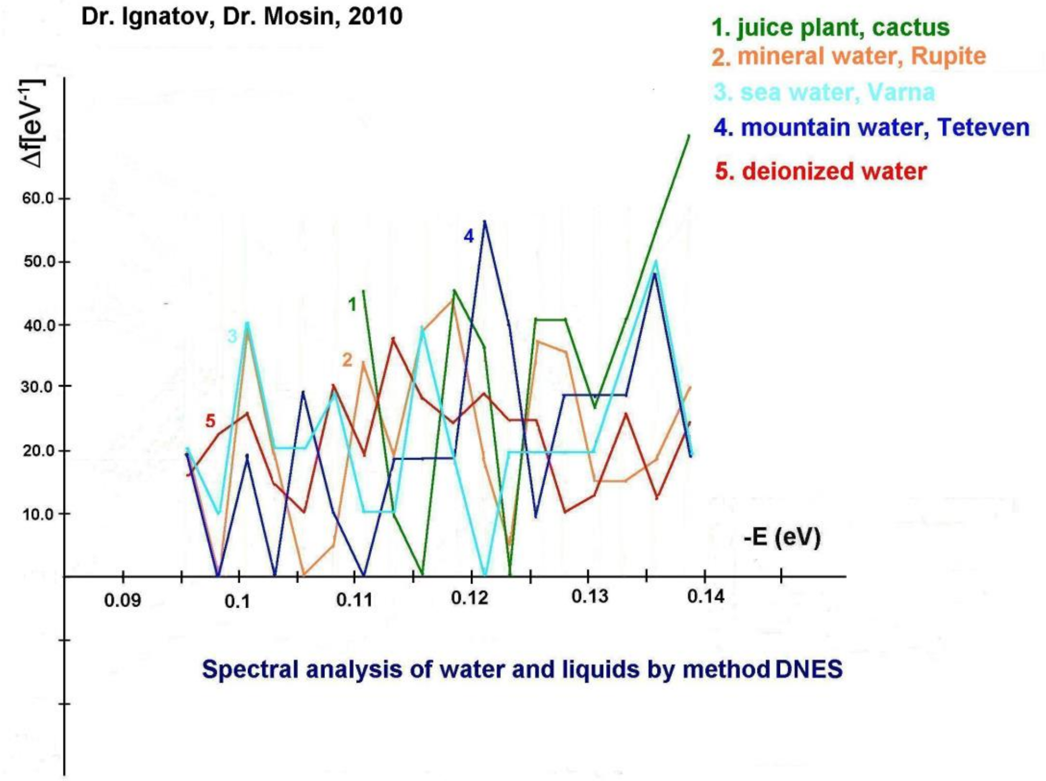


Fig. 1. DNES-spectra of water samples of various origin: 1 – the cactus juice; 2 – mineral water from Rupite village (Bulgaria); 3 – seawater (Varna, Bulgaria); 4 – mountain water (Teteven, Bulgaria); 5 – deionized water (the control)

As it was shown from these experimental data, the closest to the IR-spectrum of the cactus juice was mineral water from Rupite Village (Bulgaria), which DNES and IR spectrum is shown in Fig. 2 and Fig. 3 (Thermo Nicolet Avatar 360 Fourier-transform IR). IR-spectra of cactus juice and mineral water containing HCO_3^- (1320–1488 mg/l), Ca^{2+} (29–36 mg/l), pH (6,85–7,19), have local maximums at λ = 8,95; 9,67; 9,81; 10,47 and 11,12 μm (Fourier-IR spectrometer Brucker Vertex).

Common local maximums in the IR-spectrum between the cactus juice and seawater are detected at λ = 9,10 μm. The local maximums obtained with the IR method at λ = 9,81 μm (k = 1019 cm^{-1}) and λ = 8,95 μm (k = 1117 cm^{-1}) (Thermo Nicolet Avatar 360 Fourier-transform IR) are located on the spectral curve of the local maximum at λ = 9,7 μm (k = 1031 cm^{-1}) (Fig. 3). With the DNES method were obtained the following results – (wave length λ, μm) 8,95; 9,10; 9,64; 9,83; 10,45 and 11,15 μm, or (wave numbers, k, cm^{-1}) 897; 957; 1017; 1037; 1099 and 1117 cm^{-1}.

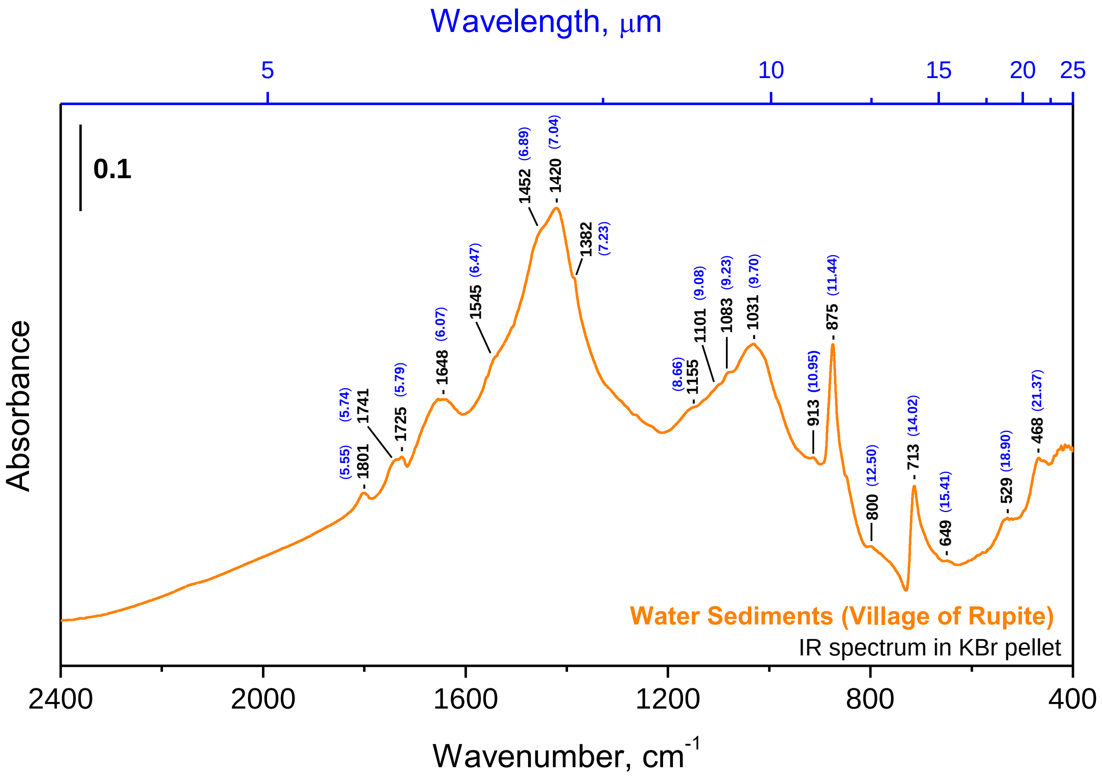


Fig. 2. IR-spectrum of water sediments obtained from Rupite Village (Bulgaria)

Table 1. Characteristics of spectra of water of various origin obtained by DNES-method*

-E, eV			λ, μm	k, cm^{-1}
Cactus juice	**Mineral water from Rupite Village (Bulgaria)**	**Seawater**		
0,1112	0,1112	–	11,15	897
0,1187	0,1187	–	10,45	957
0,1262	0,1262	–	9,83	1017
0,1287	0,1287	–	9,64	1037
0,1362	–	0,1362	9,10	1099
0,1387	0,1387	–	8,95	1117

Notes: *The function of the distribution of energies Δf was measured in reciprocal electron volts (eV^{-1}). It is shown at which values of the spectrum -E (eV) were observed the biggest local maximums of this function; λ – wave length; k – wave number.

The results with the Mediterranean jellyfish *Cotylorhiza tuberculata* indicated that the jellyfish has local maximums in IR-spectra at λ = 8,98 μm and λ = 10,18 μm (Fig. 3). Before measurements the jellyfish was kept in seawater for several days. On comparison the seawater has a local maximum at λ = 8,93 μm in IR-spectra. These results were obtained with Thermo Nicolet Avatar 360 Fourier-transform IR. With DNES method the local maximums in spectra for jellyfish are detected at λ = 8,95 and 10,21 μm, and for seawater – at λ = 9,10 μm. A differential spectrum was recorded between jellyfish and seawater by using the Thermo Nicolet Avatar 360 Fourier-transform IR method. In the IR-spectrum of jellyfish are observed more pronouncedly expressed local maximums, detected by Thermo Nicolet Avatar 360 Fourier-transform IR and DNES method. The measurements demonstrate that two common local maximums are observed in IR-spectra of jellyfish and seawater. These maximums are not observed in the IR-spectrum of cactus juice and mineral water from Rupite (Bulgaria). Jellyfish contains approximately 97 (w/w) % of water and is more unstable living organism compared to those ones formed stromatolites. The explanation for this is the smaller concentration of salts and, therefore, the smaller number of local maximums in the IR-spectrum in relation to seawater.

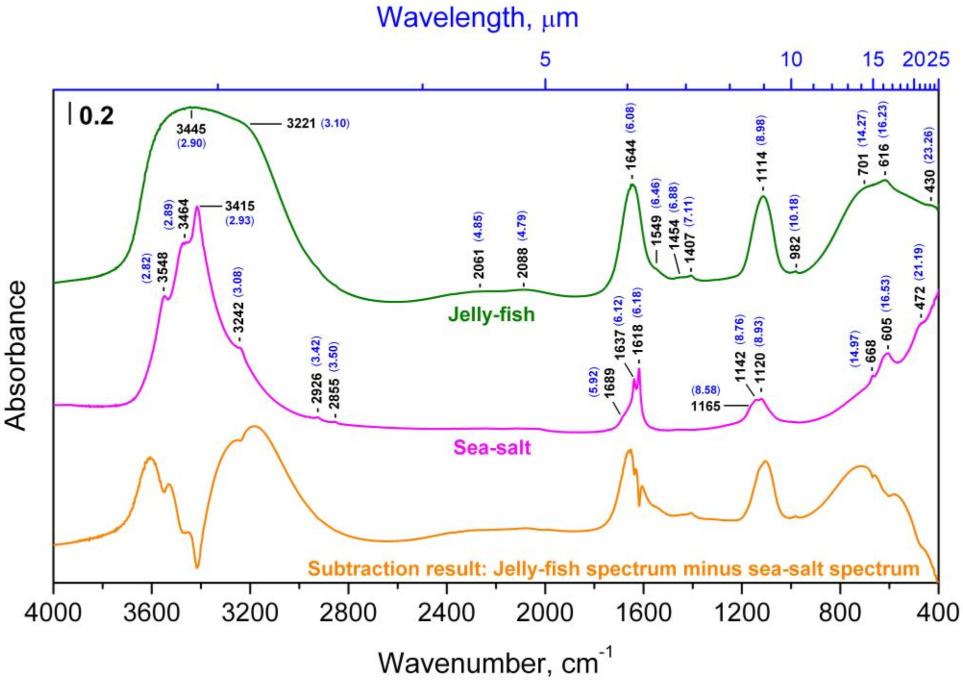


Fig. 3. IR-spectrum of seawater obtained from Varna (Bulgaria) and jellyfish *Cotylorhiza tuberculata*, Chalkida (Greece), Aegean Sea

Such a character of IR- and DNES-spectra and distribution of local maximums may prove that hot mineral alkaline water is preferable for origin and maintenance of life compared to other types of water analyzed by these methods. Thus, in hot mineral waters the local maximums in the IR-spectrum are more manifested compared to the local maximums obtained in IR-spectrum of the same water at a lower temperature. The difference in the local maximums from t = +20 °C to t = +95 °C at each 5 °C according to the Student *t*-criterion makes up $p < 0,05$. These data indicate that the origination of life and living matter depends on the structure and physical chemical properties of water, as well as its temperature and pH value. The most closed to the IR- and DNES-spectrum of water, which contains bicarbonates and calcium ions typical for the formation of stromatolites is the IR-spectrum of cactus juice. For this reason cactus juice was applied as a model system. The most closed to local maximums in IR-spectrum of cactus juice are local maximums in IR-spectra of alkaline mineral water interacting with $CaCO_3$ and then seawater. In connection with these data the following reactions participating with $CaCO_3$ in aqueous solutions are important:

$$CO_2 + 4H_2S + O_2 = CH_2O + 4S + 3H_2O, \quad (3)$$

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2, \quad (4)$$

$$CO_2 + OH^- = HCO_3^- \quad (5)$$

$$2HCO_3^- + Ca^{2+} = CaCO_3 + CO_2 + H_2O \quad (6)$$

The equation (3) shows how some chemosynthetic bacteria use energy from the oxidation of H_2S and CO_2 to S and formaldehyde (CH_2O). The equation (4) is related to one of the most common processes in nature: in the presence of H_2O and CO_2, $CaCO_3$ transforms into $Ca(HCO_3)_2$. In the presence of hydroxyl OH^- ions, CO_2 transforms into HCO_3^- (equation (5)). Equation (6) is valid for the process of formation of the stromatolites – the dolomite layered acretionary structures formed in shallow seawater by colonies of cyanobacteria. In 2010 D. Ward described fossilized stromatolites in the Glacier National Park (USA) [13]. Stromatolites aged 3,5 billion years had lived in warm and hot water in zones of volcanic activity, which could be heated by magma. This suggests that the first living forms evidently evolved in hot geysers [14]. It is known that water in geysers is rich in carbonates, while the temperature is ranged from +100 °C to +150 °C. In 2011 a team of Japanese scientists under the leadership of T. Sugawara showed that life originated in warm or, more likely, in hot water [15]. From aqueous solution of organic molecules, DNA and synthetic enzymes were created proto cells. Under experimental conditions the initial solution was heated to a temperature close to the water's boiling point +95 °C. Then the temperature was lowered to +65 °C with formation of proto cells with primitive membrane. These experiments are excellent confirmation of the possibility that first organic forms of life originated in hot water.

The above-mentioned data can predict a possible transition from synthesis of small organic molecules under the temperatures +70–100 °C to more complex organic molecules as proteins. There are reactions of condensation-dehydration of amino acids into separate blocks of peptides that occur under alkaline conditions, with pH = 9–11. The important factor in reaction of condensation of two amino acid molecules into dipeptide is allocation of H_2O molecule when a peptide chain is formed. Because the reaction of polycondensation of amino acids is accompanied by dehydration, the H_2O removal from the reaction mixture speeds up the reaction rates. This testifies that formation of early organic forms may have occured nearby active volcanoes, because at early periods of geological history volcanic activity occurred more actively than during subsequent geological times. However, dehydratation accompanies not only amino acid polymerization, but also association of other small blocks into larger organic molecules, and also polymerization of nucleotides into nucleic acids. Such association is connected with the reaction of condensation, at which from one block a proton is removed, and from another – a hydroxyl group with the formation of H_2O molecule.

In 1969 the possibility of existence of condensation-dehydration reactions under conditions of primary hydrosphere was proven by M. Calvin [16]. From most chemical substances hydrocyanic acid (HCN) and its derivatives – cyanoamid (CH_2N_2) and dicyanoamid ($HN(CN)_2$) possess dehydration ability and the ability to catalyze the process of linkage of H_2O from primary hydrosphere [17]. The presence of HCN in primary hydrosphere was proven by S. Miller's early experiments [18]. Chemical reactions with HCN and its derivatives are complex with a chemical point of view; in the presence of HCN, CH_2N_2 and $HN(CN)_2$ the condensation of separate blocks of amino acids accompanied by dehydration, can proceed at normal temperatures in strongly diluted H_2O-solutions. These reactions show the results of synthesis from separate smaller molecules to larger organic molecules of polymers, e.g. proteins, polycarboxydrates, lipids, and ribonucleic acids (Fig. 4). Furthermore, polycondensation reactions catalyzed by HCN and its derivatives depend on acidity of water solutions in which they proceed [19]. In acid aqueous solutions with pH = 4–6 these reactions do not occur, whereas alkaline conditions with pH = 9–10 promote their course. There has not been unequivocal opinion, whether primary water was alkaline, but it is probable that such pH value possessed mineral waters adjoining with basalts, i.e. these reactions could occur at the contact of water with basalt rocks, that testifies our hypothesis.

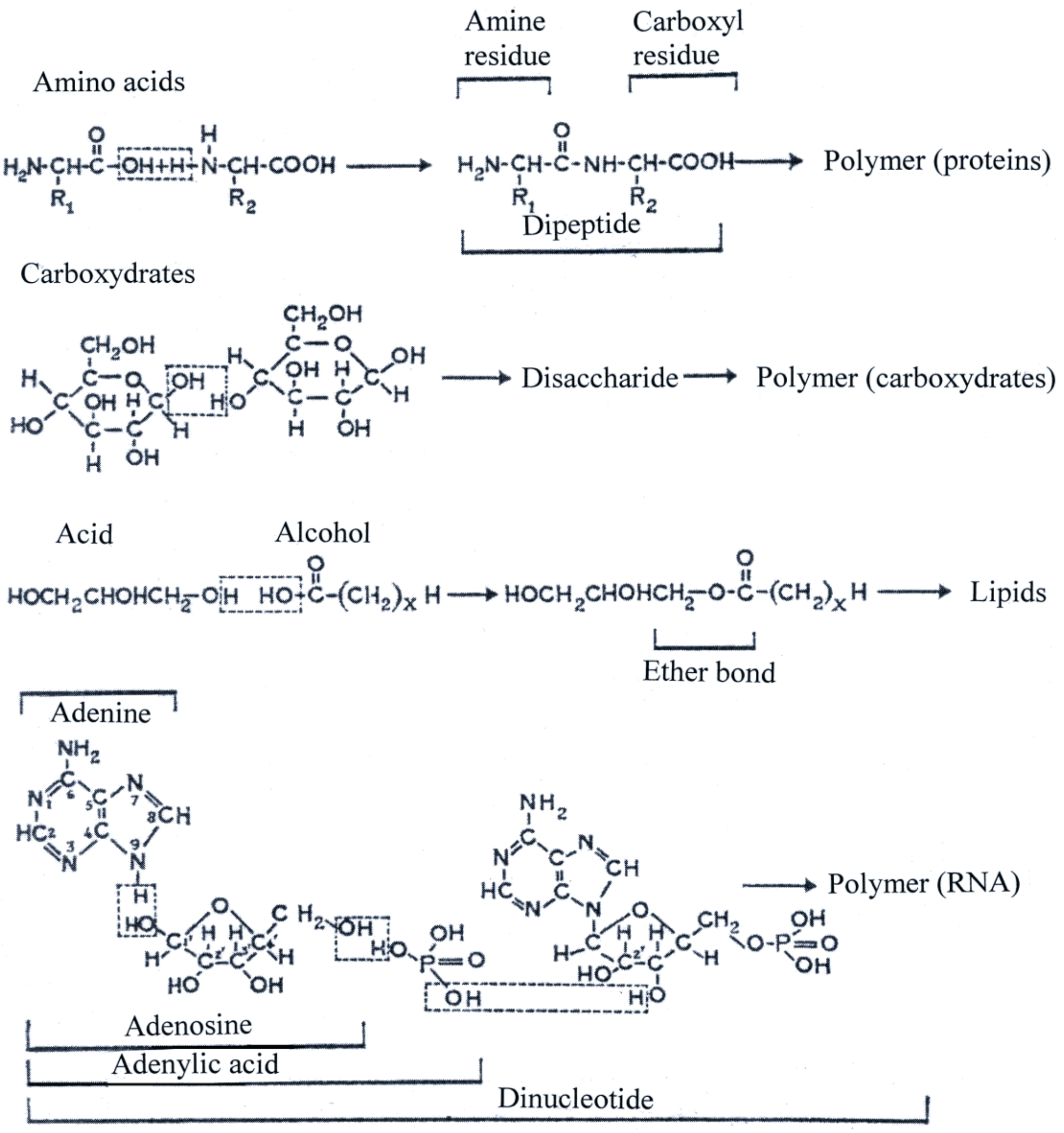
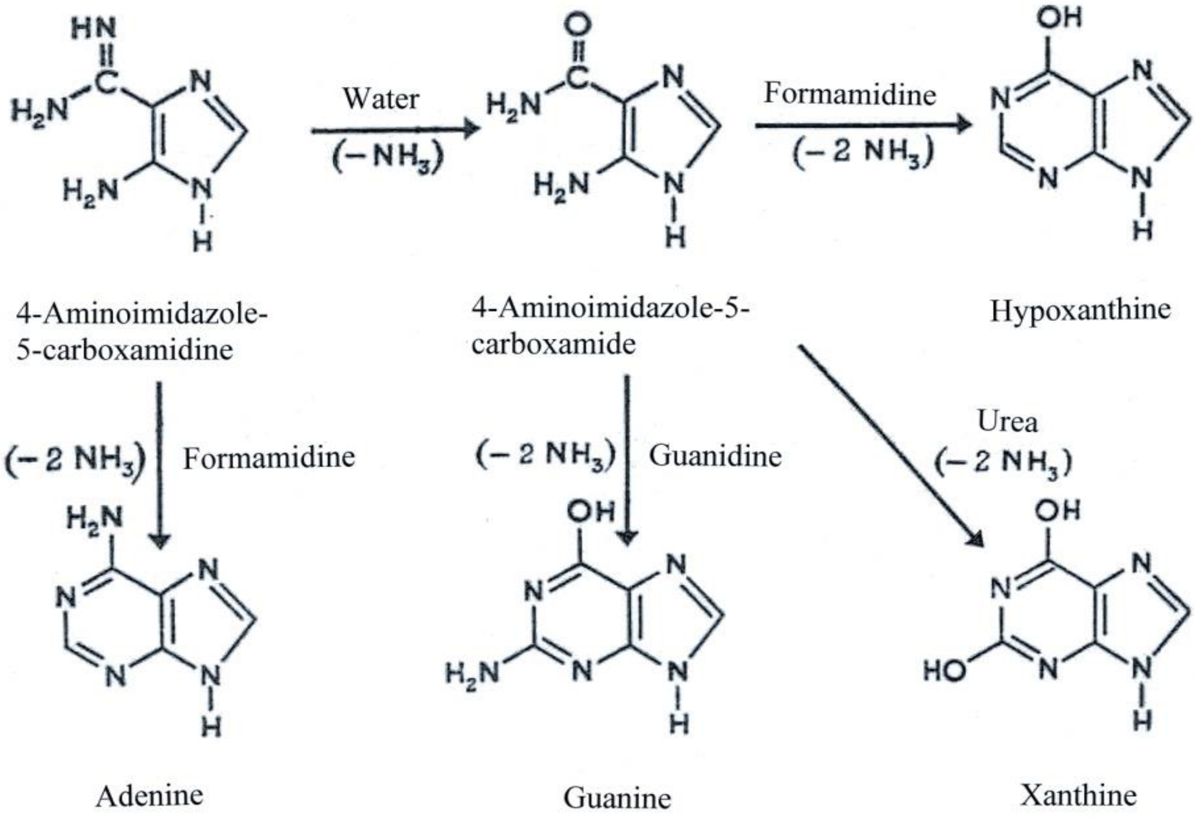
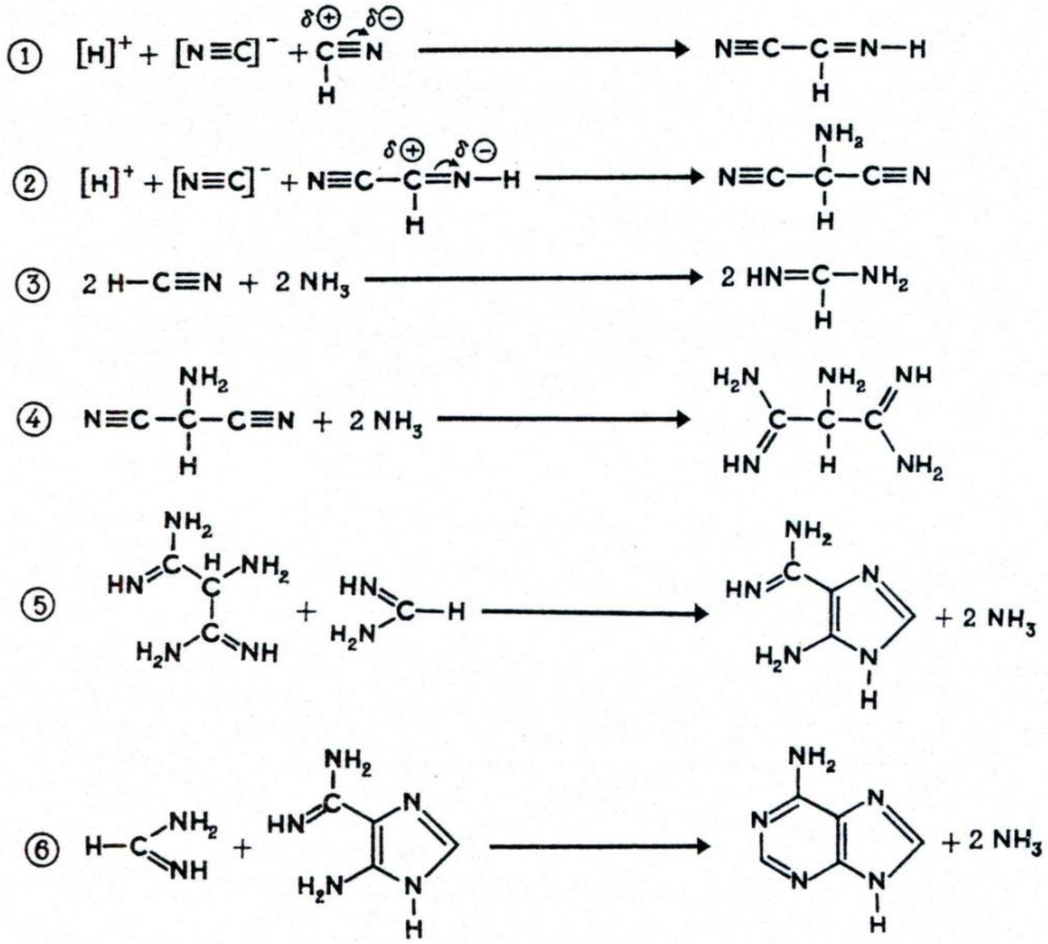


Fig. 4. Possible reactions of condensation and dehydration in alkaline conditions with pH = 9–10 catalyzed by HCN and its derivatives, resulting in synthesis from separate molecules larger organic molecules of polymers. The top three equations: condensation and the subsequent polymerization of amino acids in proteins; carbohydrates – in polycarboxydrates and acids and ethers – into lipids. The bottom equation – condensation of adenine with ribose and H_3PO_4, leading to formation of dinucleotide

It should be noted, that geothermal sources might be used for synthesis of various organic molecules. Thus, amino acids were detected in solutions of formaldehyde CH_2O with hydroxylamine NH_2OH, formaldehyde with hydrazine (N_2H_4) in water solutions with HCN, after heating of a reactionary mixture to +95 °C [20]. In model experiments the reaction products were polymerized into peptide chains that are the important stage towards inorganic synthesis of protein. In a reactionary mixture with a HCN–NH_3 solution in water were formed purines and pyrimidines (Fig. 5). In other experiments amino acid mixtures were subjected to influence of temperatures from +60 °C up to +170 °C with formation of short protein-like molecules resembling early evolutionary forms of proteins subsequently designated as thermal proteinoids. They consisted of 18 amino acids usually occurring in protein hydrolyzates. The synthesized proteinoids are similar to natural proteins on a number of other important properties, e. g. on linkage by nucleobases and ability to cause the reactions similar to those catalyzed by enzymes in living organisms as decarboxylation, amination, deamination, and oxidoreduction. Proteinoids are capable to catalytically decompose glucose [21] and to have an effect similar to the action of α-melanocyte-stimulating hormone [22]. The best results on polycondensation were achieved with the mixes of amino acids containing aspartic and glutamic acids, which are essential amino acids occurring in all modern living organisms.



a)



b)

Fig. 5. Prospective mechanisms of thermal (+95 °C) synthesis of purines in aqueous solutions:
a) – synthesis of hypoxanthine, adenine, guanine and xanthine from 4-aminoimidazole-5-carboxamidine, 4-aminoimidazole-5-carboxamide, water, NH_3, formamidine and urea;
b) – synthesis of adenine from NH_3 and HCN (total reaction: 5HCN = adenine)

Under certain conditions (temperature, pH) in hot mixture of thermal proteinoids in water solutions are formed elementary structures like proteinoid microspheres with diameter 5–10 μm [23]. The best results on polycondensation were achieved with the mixes of amino acids containing aspartic and glutamic acids, which are essential amino acids occurring in all modern living organisms. By morphological features the proteinoid microspheres with a diameter ~5–10 μm resemble cell membrane, which in certain conditions (pH = 4–5) may be double (Fig. 6). The catalyst for their formation could serve sulfur and its derivatives which were found in ancient rocks in the form of grains of sulfides, as well as pyrite sands. Synthesis of protenoid microspheres from a mixture of thermal proteinoids is important because it provides material for the next stage of the evolution of life. This is the stage from disparate organic molecules to organized proteinoid molecules having organized structure and separated from the surrounding environment by the primitive membrane.

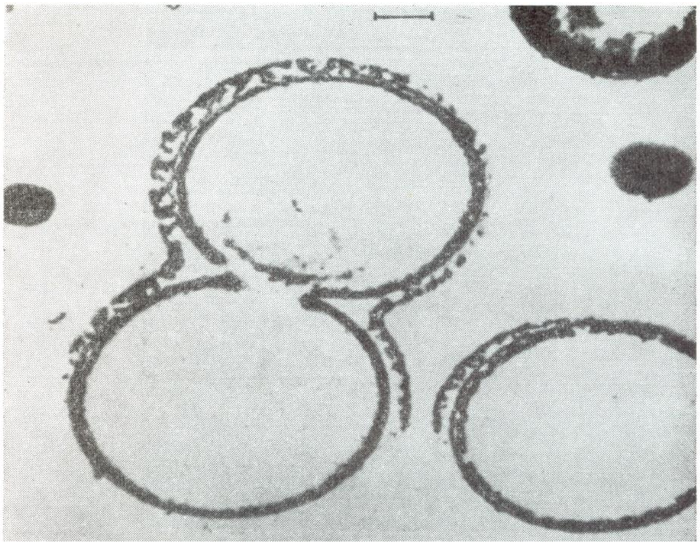


Fig. 6. Electron micrographs of sections of thermal proteinoid microspheres in scanning electron microscope (magnification × ~1000 times) (Nakashima, 1987).

In further experiments was applied gas electric discharge analogous to S. Miller's experiments [24]. The first experiments on the modeling of non-equilibrium conditions with gas electric discharge simulating primary atmosphere and electrosynthesis of organic substances from anorganic ones under the energy of the electric field in a primary oxygen-free atmosphere were held in 1953 by S. Miller (USA) [24]. For this aim the mixture of water and gases consisted of hydrogen (H_2), methane (CH_4), ammonia (NH_3) and carbon monoxide (CO) was placed into a closed glass container being exposed by pulsating electrical spark discharges at the temperature of boiling water; oxygen was not allowed into the unit. After processing the reaction mixure by the electric discharge it was found that from the initial inorganic substance was synthesized organic compounds – aldehydes and amino acids. Experiments found that approximately ~10–15% of carbon was transferred into an organic form. However, about ~2% of carbon was detected in the amino acids, the most common of which was glycine. Initial analysis showed the presence in the reaction mixture obtained after the processing by spark electric discharge 5 amino acids. A more complete analysis carried out in 2008 [25], showed the formation by electrosynthesis in the reaction mixture 22 amino acids having from 5 to 20 carbon atoms in the molecule (Fig. 7). Interestingly is that along with the amino acids in the reaction mixture after the treatment with electric spark discharges were detected trace amounts of nucleic acid precursors – nucleosides.

It should be noted that in the implementation of the gas discharge effect as well as in experiments of S. Miller are modeled extreme non-equilibrium conditions with gas electric discharge, resulting that in a thin layer of air gap with thickness ~100 μm are formed reactive radicals reacting with each other to form new compounds (electrosynthesis). Such extreme conditions are thought to have occurred in the primary oxygen-free atmosphere of the Earth, which supposedly consisted of a mixture of water and gases – H_2, CH_4, NH_3 and CO, subjected to spark electrical discharges (lightning) under the conditions of high solar (UV) and geothermal activity.

The analogous experiment was conducted by the authors under laboratory conditions. According to our previous experiments, the first living structures may have evolved in warm and hot mineral water with a high content of bicarbonate (HCO_3^-) anions, cations of alkali metals (Na^+, Ca^{2+}, Mg^{2+}, Zn^{2+}) and deuterium in the form of HDO [26]. There occurred gas electric discharge (lightning) in the primordial atmosphere close to the water surface. In the course of experiment was used the similar gas electric discharge on water drops placed on the electrode of the device for gas electric discharge formation. The similar composition and water temperature were modeled on the electrode of the gas discharge device made of hostafan, with electric voltage – 15 kV, electric impulse duration – 10 μs; electric current frequency – 15 kHz, wherein the air gap layer on the boundary with water sample was formed the electrical discharge, similar to plasma phenomena (lightning) and the electrostatic discharge on the surface of organic and inorganic samples of various kinds. Water drops were heated up to the boiling point in an electric field of high frequency and the electric discharge was applied, analogious as that in the primordial atmosphere. As a result, an organized structure with a size of 1,2–1,4 mm was formed in interelectrode space (Fig. 8). It was formed as a result of accretion of smaller elementary structures sized up 5–10 μm into the biggest structure having the size 1,2–1,4 mm and concentrated in the spase where the electric field is applied. It should be noted that no structure was organized in a control sample of water placed on the electrode. Before its placement on the electrode, the water was heated to boiling point and then cooled down. The structure organization increased with the increase of the duration of the gas electric discharge. Moreover, in experiments was observed the formation of small structures and their further "adjoining" to the larger structure. The large structure was preserved the original size for some time in the absence of the electric discharge.

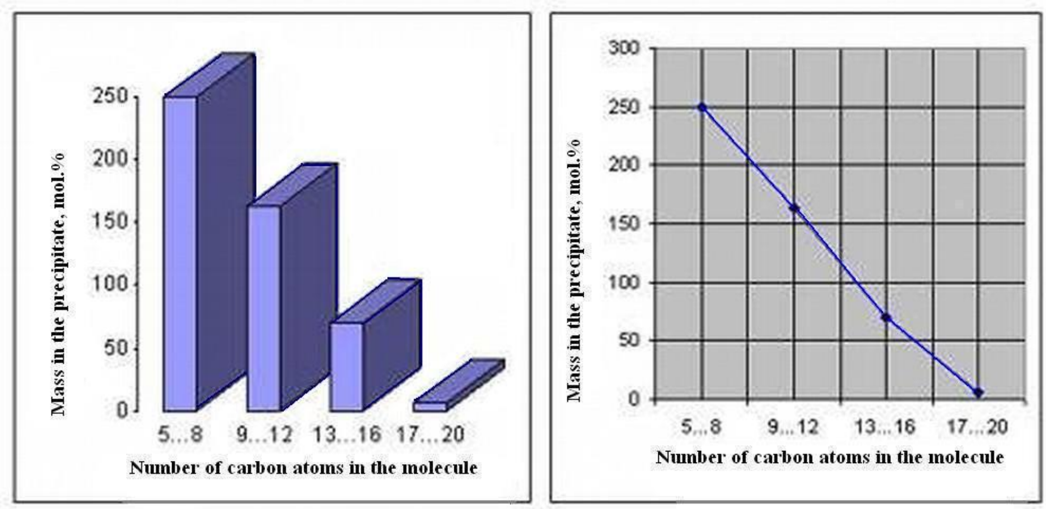


Fig. 7. Distribution of carbon compounds obtained in the experiments of S. Miller, mass and number of carbon atoms in the molecule (diagrams constructed by the authors according to the S. Miller experiments)

Fig. 8. The organized structure in water sample subjected to the temperature +100 °C in the electric field of high voltage and frequency (I. Ignatov, 2014). The material of the electrode – hostafan; the electric voltage – 15 kV, the electric impulse duration – 10 μs; the electric current frequency – 15 kHz.

This experiment shows that self-organization in water under certain external termal conditions may take place. In natural conditions water is heated up to +100 °C by the magma. The structure formed from heated water was evidently a result of self-organization. Living organisms are complex self-organizing systems. Thermodynamically they belong to the open systems because they constantly exchange substances and energy with the environment. The changes in the open systems are relatively stable in time. The stable correlation between components in an open system is called a dissipative structure. According to I. Prigozhin, the formation of dissipative structures and the elaboration to living cells is related to changes in entropy [27].

Taking into account these views it may be concluded that the initial stage of evolution, apparently, was connected with formation at high temperature of the mixtures of amino acids and nitrogenous substances – analogues of nucleic acids. Such synthesis is possible in aqueous solutions under thermal conditions in the presence of H_3PO_4. The next stage is polycondensation of amino acids into thermal proteinoids at temperatures 65–95 °C. After that in a mix of thermal proteinoids in hot water solutions were formed membrane like structures.

Our data are confirmed by experiments of T. Sugawara (Japan), who in 2011 created the membrane like proto cells from aqueous solution of organic molecules, DNA and synthetic enzymes under temperature close to the water boiling point +95 °C [28]. This data confirm the possibility that first organic forms of life originated in hot water.

IR-Spectroscopy of Water with Varying Content of Deuterium

Numerous studies carried out by us with various biological objects in D_2O, proved that when biological objects being exposed to water with different deuterium content, their reaction varies depending on the isotopic composition of water (the content of deuterium in water) and magnitude of isotope effects determined by the difference of constants of chemical reactions rates k_H/k_D in H_2O and D_2O. The maximum kinetic isotopic effect observed at ordinary temperatures in chemical reactions leading to rupture of bonds involving hydrogen and deuterium atoms lies in the range $k_H/k_D = 5–8$ for C–H versus C–D, N–D versus N–D, and O–D versus bonds [29].

The chemical structure of D_2O molecule is analogous to that one for H_2O, with small differences in the length of the covalent H–O-bonds and the angles between them. The molecular mass of D_2O exceeds on 10% that one for H_2O. The difference in nuclear masses stipulates the isotopic effects, which may be sufficiently essential for the $^1H/D$ pair. As a result, physical-chemical properties of D_2O differ from H_2O: D_2O boils at t = +101,44 °C, freezes at t = +3,82 °C, has maximal density at t =+11,2 °C (1,106 g/cm^3) [30]. In mixtures of ^2H_2O with H_2O the isotopic exchange occurs with high speed with the formation of semi-heavy water (^1HDO): $D_2O + H_2O = {}^1HDO$. For this reason deuterium presents in smaller content in aqueous solutions in form of ^1HDO, while in the higher content – in form of D_2O. The chemical reactions in D_2O are somehow slower compared to H_2O. D_2O is less ionized, the dissociation constant of D_2O is smaller, and the solubility of the organic and inorganic substances in D_2O is smaller compared to these ones in H_2O. Due to isotopic effects the hydrogen bonds with the participation of deuterium are slightly stronger than those ones formed of hydrogen.

The comparative analysis of IR-spectra of H_2O solutions and its deuterated analogues (D_2O, HDO) is of considerable interest for biophysical studies, because at changing of the atomic mass of hydrogen by deuterium atoms in H_2O molecule their interaction will also change, although the electronic structure of the molecule and its ability to form H-bonds, however, remains the same. The IR spectra of water usually contain three absorption bands, which can be identified as 1 – absorption band of the stretching vibration of OH^- group; 2 – absorption band of the first overtone of the bending vibration of the molecule HDO; 3 – absorption band of stretching vibration of OD^- group. OH^- group is able to absorb much infrared radiation in the infrared region of the IR-spectrum. Because of its polarity, these groups typically react with each other or with other polar groups to form intra-and intermolecular hydrogen bonds. The hydroxyl groups not involved in formation of hydrogen bonds are usually given the narrow bands in IR spectrum and the associated groups – broad intense absorption bands at lower frequencies. The magnitude of the frequency shift is determined by the strength of the hydrogen bond. Complication of the IR spectrum in the area of OH^- stretching vibrations can be explained by the existence of different types of associations, a manifestation of overtones and combination frequencies of OH^- groups in hydrogen bonding, as well as the proton tunneling effect (on the relay mechanism. Such complexity makes it difficult to interpret the IR spectrum and partly explains the discrepancy in the literature available on this subject.

The local maximums in IR-spectra reflect vibrational-rotational transitions in the ground electronic state; the substitution with deuterium changes the vibrational-rotational transitions in H_2O molecule that is why it appears other local maximums in IR-spectra. In the water vapor state, the vibrations involve combinations of symmetric stretch (v_1), asymmetric stretch (v_3) and bending (v_2) of the covalent bonds with absorption intensity (H_2O) v_1;v_2;v_3 = 2671; 1178,4; 2787,7 cm^{-1}. For liquid water absorption bands are observed in other regions of the IR-spectrum, the most intense of which are located at 2100 cm^{-1} and 710–645 cm^{-1}. For D_2O molecule these ratio compiles 2723,7; 1403,5 and 3707,5 cm^{-1}, while for HDO molecule – 2671,6; 1178,4 and 2787,7 cm^{-1}. HDO (50 mole% H_2O + 50 mole% ^2H_2O; ~50 % HDO, ~25 % H_2O, ~25 % D_2O) has local maxima in IR-spectra at 3415 cm^{-1}, 2495 cm^{-1} 1850 cm^{-1} and 1450 cm^{-1} assigned to OH^- -stretch, OD^- -stretch, as well as combination of bending and libration and HDO bending respectively.

In the IR-spectrum of liquid water absorbance band considerably broadened and shifted relative to the corresponding bands in the spectrum of water vapor. Their position depends on the temperature [31]. The temperature dependence of individual spectral bands of liquid water is very complex. Furthermore, the complexity of the IR-spectrum in the area of OH^- stretching vibration can be explained by the existence of different types of H_2O associations, manifestation of overtones and composite frequencies of OH^- groups in the hydrogen bonds, and the tunneling effect of the proton (for relay mechanism). Such complexity makes it difficult to interpret the spectrum and partly explains the discrepancy in the literature available on this subject.

In liquid water and ice the IR-spectra are far more complex than those ones of the vapor due to vibrational overtones and combinations with librations (restricted rotations, i.g. rocking motions). These librations are due to the restrictions imposed by hydrogen bonding (minor L_1 band at 395,5 cm^{-1}; major L_2 band at 686,3 cm^{-1}; for liquid water at 0 ^oC, the absorbance of L_1 increasing with increasing temperature, while L_2 absorbance decreases but broadens with reduced wave number with increasing temperature [32]. The IR spectra of liquid water usually contain three absorbance bands, which can be identified on absorption band of the stretching vibration of OH^- group; absorption band of the first overtone of the bending vibration of the molecule HDO and absorption band of stretching vibration of OD^- group. Hydroxyl group OH^- is able to absorb much infrared radiation in the infrared region of the IR-spectrum. Because of its polarity, these groups typically react with each other or with other polar groups to form intra- and inter-molecular hydrogen bonds. The hydroxyl groups, which are not involved in formation of hydrogen bonds, usually produce the narrow bands in IR spectrum, while the associated groups – broad intense absorbance bands at lower frequencies. The magnitude of the frequency shift is determined by the strength of the hydrogen bond. Complication of the IR spectrum in the area of OH^- stretching vibrations can be explained by the existence of different types of associations of H_2O molecules, a manifestation of overtones and combination frequencies of OH^- groups in hydrogen bonding, as well as the proton tunneling effect (on the relay mechanism).

Assignment of main absorbtion bands in the IR-spectrum of liquid water is given in Table 2. The IR spectrum of H_2O molecule was examined in detail from the microwave till the middle (4–17500 cm^{-1}) visible region and the ultraviolet region – from 200 nm^{-1} to ionization limit at 98 nm^{-1} [33]. In the middle visible region at 4–7500 cm^{-1} are located rotational spectrum and the bands corresponding to the vibrational-rotational transitions in the ground electronic state. In the ultraviolet region (from 200 nm^{-1} to 98 nm^{-1}) are located bands corresponding to transitions from the excited electronic states close to the ionization limit in the electronic ground state. The intermediate region of the IR-spectrum – from 570 nm to 200 nm corresponds to transitions to higher vibrational levels of the ground electronic state.

Table 2. The assignment of main frequencies in IR-spectra of liquid water H_2O and D_2O

Main vibrations of liquid H_2O and ^2H_2O				
Vibration(s)	**H_2O (t = 25 °C)**		**D_2O (t = 25 °C)**	
	ν, cm^{-1}	**E_0, M^{-1} cm^{-1}**	**ν, cm^{-1}**	**E_0, M^{-1} cm^{-1}**
Spinning ν_1 + deformation ν_2	780–1645	21,65	1210	17,10
Composite $\nu_1 + \nu_2$	2150	3,46	1555	1,88
Valence symmetrical ν_1, valence asymmetrical ν_3, and overtone $2\nu_2$	3290–3450	100,65	2510	69,70

Results of IR-spectroscopy with Infra Spec VFA-IR device show that at λ = 4,1 μm, even at low concentrations of deuterium of 0,35 and 0,71%, there is observed a decline in the local maximums relative to the local maximum of 100% pure water (the local maximums in IR-spectra reflect vibrational-rotational transitions in the ground electronic state because at changing the atomic mass of hydrogen and deuterium atoms in the water molecule their interaction will also change, although the electronic structure of the molecule and its ability to form H-bonds, however, remains the same; with the substitution with deuterium the vibrational-rotational transitions are changed, that is why it appears other local maximums in IR-spectra. The result is reliable regarding the content of deuterium in natural waters from 0,015–0,03%.

At further transition from H_2O monomers to H_4O_2 dimmer and H_6O_3 trimmer absorption maximum of valent stretching vibrations of the O–H bond is shifted toward lower frequencies (ν_3 = 3490 cm^{-1} and ν_1 = 3280 cm^{-1}) [34] and the bending frequency increased (ν_2 = 1644 cm^{-1}) because of the hydrogen bonding. The increased strength of hydrogen bonding typically shifts the stretch vibration to lower frequencies (red-shift) with greatly increased intensity in the infrared due to the increased dipoles. In contrast, for the deformation vibrations of the H–O–H, it is observed a shift towards higher frequencies. Absorption bands at 3546 and 3691 cm^{-1} were attributed to the stretching modes of the dimmer [$(H_2O)_2$]. These frequencies are significantly lower than the valence modes of ν_1 and ν_3 vibrations of isolated H_2O molecules at 3657 and 3756 cm^{-1} respectively). The absorption band at 3250 cm^{-1} represents overtones of deformation vibrations. Among the frequencies between 3250 and 3420 cm^{-1} it is possible the Fermi resonance (this resonance is a single substitution of intensity of one fluctuation by another fluctuation when they accidentally overlap each other). The absorption band at 1620 cm^{-1} is attributed to the deformation mode of the dimmer. This frequency is slightly higher than the deformation mode of the isolated H_2O molecule (1596 cm^{-1}). A shift of the band of deformation vibration of water in the direction of high frequencies at the transition from a liquid to a solid state is attributed by the appearance of additional force, preventing O–H bond bending. The deformation absorption band in IR-spectrum of water has a frequency at 1645 cm^{-1} and very weak temperature dependence. It changes little in the transition to the individual H_2O molecule at a frequency of 1595 cm^{-1}. This frequency is found to be sufficiently stable, while all other frequencies are greatly affected by temperature changes, the dissolution of the salts and phase transitions. It is believed that the persistence of deformation oscillations is stipulated by processes of intermolecular interactions, e.g. by the change in bond angle as a result of interaction of H_2O molecules with each other, as well as with cations and anions.

Thus, the study of the characteristics of the IR spectrum of water allows to answer the question not only on the physical parameters of the molecule and the covalent bonds at isotopic substitution with deuterium, but also to make a certain conclusion on associative environment in water. The latter fact is important in the study of structural and functional properties of water associates and its isotopomers at the isotopic substitution with deuterium. The substitution of H with D affects the stability and geometry of hydrogen bonds in an apparently rather complex way and may through the changes in the hydrogen bond zero-point vibration energies, alter the conformational dynamics of hydrogen (deuterium)-bonded structures of macromolecules as DNA and proteins in D_2O.

Conclusion

The data obtained testify that origination of first organic forms of life depends on physical-chemical properties of water and external factors – temperature, pH, electric discharges and isotopic composition. Hot mineral alkaline water interacting with $CaCO_3$ is most closed to these conditions. Next in line with regard to its quality is seawater. For chemical reaction of dehydration-condensation to occure in hot mineral water, water is required to be alkaline with the pH ranged 9–11. In warm and hot mineral waters the local maximums in IR-spectra from 8 to 14 μm were more expressed in comparison with the local maximums measured in the same water samples with lower temperature. The content of deuterium in hot mineral water may be increased due to the physical chemical processes of the deuterium accumulation stipulated by the solar radiation, volcanic geothermal processes and electric discharges in the atmosphere. These natural processes could lead to the enrichment of the hydrosphere by deuterium in the form of HDO which evaporates more slowly than H_2O, but condenses faster. If the primary hydrosphere really contained HDO, that this may explain the thermal stability of the first organic life forms in the hot mineral water, as the thermal stability of deuterated macromolecules like DNA and proteins in D_2O solutions is somewhat higher than their protonated forms due to isotopic effects of deuterium.

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Реакции конденсации-дегидратации в водных щелочных растворах со значением pH = 9–11 и температурах t = 65–95 °C в процессе моделирования первичной гидросферы

[1] Игнат Игнатов
[2] Олег Викторович Мосин

[1] Научно-исследовательский центр медицинской биофизики (РИЦМБ), Болгария
Профессор, доктор наук Европейской академии естественных наук (ФРГ), директор НИЦМБ
1111 София, ул. Н. Коперника, 32/6
E-mail: mbioph@dir.bg
[2] Московский государственный университет прикладной биотехнологии, Российская Федерация
Старший научный сотрудник кафедры биотехнологии, кандидат химических наук
103316 Москва, ул. Талалихина, 33
E-mail: mosin-oleg@yandex.ru

Аннотация. Рассмотрены реакции конденсации-дегидратации в щелочных водных растворах со значением pH = 9–11 и температурах t = 65–95 °C, результатом которых является синтез из мелких молекул более крупных органических молекул полимеров как короткие полипептиды в процессе моделирования первичной гидросферы, а также механизмы аккумуляции дейтерия в форме HDO в горячей минеральной воде. Для этой цели проведены исследования горячей минеральной и морской воды из Болгарских источников методами ИК- и ДНЭС-спектроскопии. В качестве модельных систем использовали сок кактуса *Echinopsis pachanoi* и средиземноморскую медузу *Cotylorhiza tuberculata*. Показано, что горячие минеральные воды с температурой от +65 °C до +95 °C и значением pH от 9 до 11 более пригодны для возникновения жизни, чем другие исследованные образцы воды. В горячей минеральной воде локальные максимумы в ИК-спектре проявлялись больше всего, по сравнению с локальными максимумами в ИК-спектре той же воды при более низкой температуре. Разница в локальных максимумах от +20 °C до +95 °C при увеличении температуры на каждый +5 °C составила в соответствии с *t*-критерием Стьюдента $p < 0,05$.

Ключевые слова: дейтерий, гидросфера, эволюция, возникновение жизни, ИК-спектроскопия, ДНЭС.