Journal of Chemical Technology and Metallurgy, 58, 2, 2023, 340-346

HISTORY-DEPENDENT HYDROGEN BONDS ENERGY DISTRIBUTIONS IN NaCl AQUEOUS SOLUTIONS UNDERGOING OSMOSIS AND DIFFUSION THROUGH A CERAMIC BARRIER

Dimitar Mehandjiev[1], Ignat Ignatov[2], Nikolai Neshev[3], Paunka Vassileva[1],
Georgi Gluhchev[4], Fabio Huether[5], Christos Drossinakis[6]

[1]Institute of General and Inorganic Chemistry
Bulgarian Academy of Sciences
Acad. G. Bonchev str., bl. 11, Sofia 1113, Bulgaria
[2]Scientific Research Center of Medical Biophysics
N. Kopernik str., 32, Sofia 1111, Bulgaria
[3]Faculty of Physics, Sofia University "St. Kliment Ohridski"
Sofia 1000, Bulgaria
[4]Institute of Information and Communication Technologies
Bulgarian Academy of Science
Acad. G. Bonchev str., bl. 2, Sofia 1113, Bulgaria
[5]EVODROP AG, Zürich, Switzerland
[6]IAWG-INTERNATIONALE Akademie für Wissenschaftliche Geistheilung
Frankfurt, Germany; Hauptplatz 44, A-2293 Marchegg, Austria
E-mail: mbioph@abv.bg

Received 01 September 2022
Accepted 20 December 2022

ABSTRACT

An investigation of simultaneous osmosis and diffusion was conducted in a setup consisting of a cylindrical ceramic element initially filled with 0.9 % sodium chloride (NaCl) aqueous solution and immersed a beaker initially filled with deionized water. The cylindrical element was made of kaolin with chemical composition Al_2O_3 (52 %) SiO_2 (47 %) Na_2O (0.3 %) K_2O (0.7 %) and pore size of 0.1 - 0.2 µm The levels of both liquids were the same at the start of the experiment and their ionic concentrations were monitored by measuring electrical conductivity with two identical meters with fixed probes in the corresponding sections. At a temperature of 20.4°C, the final equilibrium occurred in 339 hours. Subsequently, the hydrogen bonds energy distributions of the two sulutions already with equal sodium chloride (NaCl) concentrations were measured with the methods of Non-equilibrium Energy Spectrum (NES) and Differential Non-equilibrium Energy Spectrum (NES). Distinct differences between the spectra were found in the whole range of (-E) from 0.0937 to 0.1387 eV, particularly at (0.1112 eV) (λ = 11.15 µm) (ṽ = 897 cm^{-1}) eV and (0.1362 eV) (λ = 11.15 µm) (ṽ = 897 cm^{-1}). In addition, the average strength of hydrogen bonds in the ceramic element was calculated as greater than that in the beaker.

Keywords: *osmosis, diffusion, electric conductivity, hydrogen bonds, energy.*

INTRODUCTION

Treatment with ceramics has previously been shown to induce distinct changes in water structure. Sato et al. investigated such changes caused by high-temperature kaolinite ceramics using thermally simulated depolarized current, temperature profiles analysis of iced treated water and ^{1}H-NMR spectrometry [1]. They observed positive charging of the water flow due to formation of a double layer interface between it and the ceramics. In addition, they proved that the treated water reduced *E. coli* growth in poor nutritional culture media and production of cellulose by the CFG-002 bacterium, as well as suppressed the oxidation action of hydrogen peroxide.

A later work by Kozumi and Kitagawa has demonstrated ceramics-induced water structure changes by detection of increased permeability through aquapourin [2]. They used ceramics made by melting and mixing of iron and clay. Due to the treated water, the authors also observed increased proliferation of cultured human skin cells and prolonged shelf life of *Begonia* flowers. Their general explanation of these findings was based on the possibility of treated water to easily form single-file molecular structures.

Recently Kujawa et al. studied water behavior in contact with modified chemically selected powders of lantanide oxides (CeO_2, Pr_6O_{11}, Nd_2O_3 and Gd_2O_3) by goniometric, adhesion and spreading pressure measurements [3]. Thus, highly and super-hydrophobic materials with tubnable adhesive properties and fractal-like structures were developed with high efficiency (67 - 84 %). According to the authors, their method allows for production of stable materials with a wide range of potential applications in chemistry and engineering by inducing structural changes through surface interactions.

Taking all above into account, other special properties of ceramics could be expected to appear also during non-destructive chemical and physical processes in their volume.

Osmosis is the spontaneous diffusion of solvent molecules through a selectively permeable barrier from a region of lower solute concentration to a region of higher solute concentration that tends to equalize the solute concentrations on both sides of the barrier. Osmosis increases the pressure in the region of high solute concentration with respect to that in the low solute concentration region. If the barrier, to some degree, is also permeable for the solute, its molecules can simultaneously diffuse into the region of lower solute concentration. Thus, the interplay of these two opposite processes ultimately brings about equal solution concentration and pressure on both sides of the barrier. Its timing is mainly determined by the pore size of the barrier material.

The aim of the present work was to investigate the hydrogen bonds energy distributions in NaCl aqueous solutions undergoing simultaneous osmosis and diffusion through a ceramic barrier with patented ceramic element [4].

EXPERIMENTAL

Materials and Methods

The investigation was carried out with a cyllindrical ceramic element that was standardized according to BDS with an active patent BDS 70751968 . It was made of kaolin and had a filter element EFKTS 90-250 (BDS 7075-68) [4]. The chemical composition of kaolin is Al_2O_3 (52 %), SiO_2 (47 %), Na_2O (0.3 %), K_2O (0.7 %) with pore size of 0.1 - 0.2 μm. A 0.9 % NaCl solution was placed in the ceramic element. The beaker is with 770 mL of water and the ceramic element is with 350 mL of the physiological solution. The beaker is with capacity 2000 mL and ceramic element with 600 mL. The width of the membrane is 4 mm with incide diameter 65 mm. The levels of the liquids in both vessels were initially equalized. The setup was kept hermetically sealed at 20.4^{o}C.

The changes in ionic concentrations in both vessels were monitored through the changes in electrical conductivity measured with the fixed AD 76309 probes of two identical ADWA AD330 EC meters. The amount of sodium ions (Na^+) in both solutions was measured in a licensed laboratory (Eurotest Control, Sofia, Bulgaria).

The distribution of hydrogen bonds energies in the investigated solutions was measured with an optical method invented by Antonov, based on the non-equilibrium process of droplets evaporation [5]. Its output is the so-called Non-equilibrium Energy Spectrum (NES), described by a function f(E) where the energy E is expressed in eV [6 - 8]. There were results of comparison of chemical composition of medicinal plants and local maxima with methods NES and DNES [9 - 11]. Ten sample droplets and ten deionized water control droplets evaporated simultaneously on a thin BoPET film over a glass plate in a hermetic chamber. During the measurements, the temperature inside the chamber was 23.0 ± 1.0^{o}C. All investigated droplets were irradiated by parallel beams of monochromatic light (λ = 580 ± 7 nm) that fell perpendicularly to the BoPET film and the glass plate (Fig. 1). Wetting angles Θ in the range from 72.3 to 0 degrees and corresponding to hydrogen bonds energies in the range for E from -0.08 to -0.1387 eV were measured every 10 minutes for 3 hours until complete evaporation.

Subsequently, the average distribution of wetting angles f(θ) and the normalized distribution of hydrogen bonds energies f(E) were calculated as follows:

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

where E is the energy corresponding to a particular value

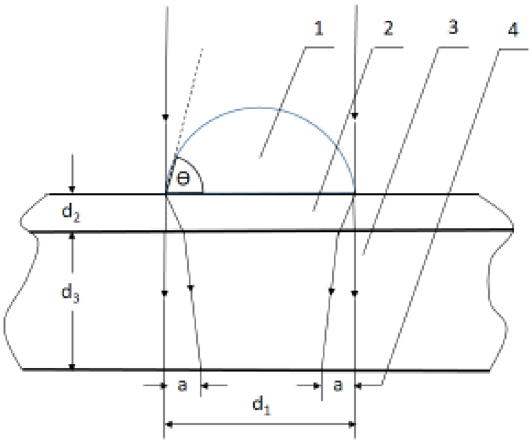

Fig. 1. Wetting angle measurement: 1 - droplet, 2 - thin BoPET film, 3 - glass plate, 4 - refraction ring width (**a**). The wetting angle θ is a function of **a** and $\mathbf{d}_3$.

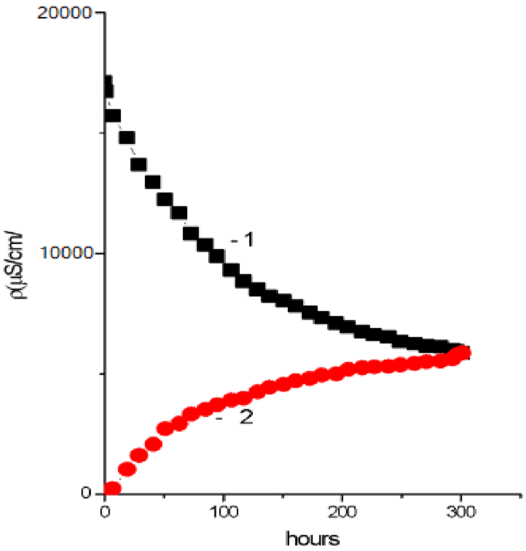

Fig. 2. Electrical conductivity of the investigated solutions vs. time: 1 - in the ceramic element, 2 - in the beaker.

of the wetting angle θ**,** and b depends on the number of water molecules per unit area at the surface layer, on the water surface tension and the initial wetting angle of the corresponding droplet.

The energy E is measured in electron volts (eV) and f(E) is called energy distribution spectrum. The water state spectrum is obtained from the non-equilibrium process of evaporation of water drops and, due to this, the term Non-equilibrium spectrum of water (NES) is used. The difference:

$$\Delta f\,(E) = f\,(\text{sample})\ \ f\,(\text{control sample}) \qquad (2)$$

is called Differential non-equilibrium energy spectrum (DNES). DNES is a measure of alteration of water structure as a result of a certain influencing factor. The combined effect of all other influencing factors besides the examined one is the same for the control and the sample, that is why it is canceled out. NES and DNES are measured in eV^{-1}.

RESULTS AND DISCUSSION

In the simultaneous processes of osmosis and diffusion, the measurements were carried out until the electrical conductivity of the two solutions reached equilibrium in 14 days and 3 hours (or 339 hours) (Fig. 2).

Conductivity increased in the beaker. The difference between the start and the end of the process was 11.24±0.11 mS cm^{-1}. In the ceramic element, conductivity decreased. The difference was (-11.24±0.11) mS cm^{-1}. The absolute values of the slopes of the two curves were different because of the different volumes of the corresponding solutions.

A process of osmosis was observed from the beaker to the ceramic cup, as shown in Table 1.

A process of diffusion was observed from the ceramic element to the beaker, as shown in Table 2.

The concentration of sodium ions (Na^+) in the ceramic element decreased from 3330 ± 330 mg L^{-1} to 1230 ± 123 mg L^{-1}. In this process, pH increased from 5.77 to 6.08

Table 1. Solution characteristics in the ceramic element.

	Na^+ (mg L^{-1})	pH	μS cm^{-1}
Initial sample 1 (0.9 % NaCl)	3330 ± 330	5.77 ± 0.11	17110
Final sample (after osmosis)	1230 ± 123	6.08 ± 0.11	5870
Difference	2100 ± 210	- 0.31	11240

Table 2. Solution characteristics in the beaker.

	Na^+ (mg.L^{-1})	pH	µS.cm^{-1}
Initial sample (deionized water)	< 2.0	6.53 ± 0.11	8.0
Final sample (after diffusion)	1140 ± 115	6.23 ± 0.11	5870
Difference	1140 ± 115	0.3	-5862

Table 3. Non-equilibrium Energy Spectra (NES) of the solution in the ceramic element.

-E(eV) x-axis	Final (after osmosis and diffusion) f (E)(eV^{-1})	Initial (0.9 % NaCl) f (E)(eV^{-1})	-E(eV) x-axis	Final (after osmosis and diffusion) f (E)(eV^{-1})	Initial (0.9 % NaCl) f (E)(eV^{-1})
0.0937	0	0	0.1187	33.3	50.2
0.0962	0	0	0.1212	**66.7**	**50.2**
0.0987	0	50.2	0.1237	0	0
0.1012	0	50.2	0.1262	33.3	25.1
0.1037	0	50.2	0.1287	33.3	25.1
0.1062	0	50.2	0.1312	0	25.1
0.1087	0	0	0.1337	33.3	25.1
0.1112	**66.7**	**0**	0.1362	33.3	0
0.1137	0	0	0.1387	**66.7**	**50.2**
0.1162	33.3	0	–	–	–

Table 4. Non-equilibrium Energy Spectra (NES) of the solution in the beaker.

- E(eV) x-axis	Final (after osmosis and diffusion) f (E)(eV^{-1})	Initial (Deionized water) f (E)(eV^{-1})	-E(eV) x-axis	Final (after osmosis and diffusion) f (E)(eV^{-1})	Initial (Deionized water) f (E)(eV^{-1})
0.0937	0	0	0.1187	0	0
0.0962	40.2	14.8	0.1212	**40.2**	**29.6**
0.0987	0	14.8	0.1237	0	29.6
0.1012	20.1	29.6	0.1262	20.1	44.4
0.1037	60.3	0	0.1287	20.1	44.4
0.1062	40.2	44.4	0.1312	20.1	14.8
0.1087	40.2	29.6	0.1337	20.1	44.4
0.1112	**0**	**0**	0.1362	0	14.8
0.1137	20.1	29.6	0.1387	**40.2**	**14.8**
0.1162	20.1	0	–	–	–

(or by 0.31 ± 0.01) due to the increased concentration of OH^- ions. The concentration of sodium ions (Na^+) in the beaker increased from < 2 to 1140 ± 115 mg L^{-1}. In this process, pH decreased from 6.53 to 6.23 (or by 0.30 ± 0.01) due to the increased concentration of H^+ ions.

At equal conductivity in the ceramic element and beaker, the amounts of sodium (Na^+) are 1140 ± 115 mg L^{-1} and 1230 ± 123 mg L^{-1}. The difference of 1230-1140 = 90 mg L^{-1}. The difference is in the statistical error. The conclusion is that there is full exchange of the sodium ions in the processes of osmosis and diffusion.

All results clearly demonstrated the obtained final equilibrium of both osmosis and diffusion.

The Non-equliblrium energy spectra (NES) of the solutions in the ceramic element and the beaker at the beginning and at the end of the experiment are presented in Table 3 and Table 4. They show distinct differences in the values of the local maxima that can be explained with the differences in ionic content.

In addition the average hydrogen bond energies calculated with NES and DNES for these solutions are shown in Table 5.

Table 5. Average hydrogen bonds energies of the sulutions in the ceramic element and the beaker.

Location	Initial NES E [eV]	Final NES E [eV]	DNES E [eV]
Ceramic element	-0.1138	-0.1181	-0.0043
Beaker	-0.1158	-0.1146	0.0012

Table 6. Non-equilibrium Energy Spectra (NES) of the solutions in the beaker and the ceramic element after the occurrence of equilibrium.

-E(eV) x-axis	Final In the beaker f (E)(eV^{-1})	Final In the ceramic element f (E)(eV^{-1})	-E(eV) x-axis	Final In the beaker f (E)(eV^{-1})	Final In the ceramic element f (E)(eV^{-1})
0.0937	0	0	0.1187	0	33.3
0.0962	40.2	0	0.1212	**40.2**	**66.7**
0.0987	0	0	0.1237	0	0
0.1012	20.1	0	0.1262	20.1	33.3
0.1037	40.2	0	0.1287	20.1	33.3
0.1062	60.3	0	0.1312	20.1	0
0.1087	40.2	0	0.1337	20.1	33.3
0.1112	**0**	**66.7**	0.1362	0	33.3
0.1137	20.1	0	0.1387	**40.2**	**66.7**
0.1162	20.1	33.3	–	–	–

Consequently, the average strength of hydrogen bonds was increased in the ceramic cup (due to the influx of water molecules) and decreased in the beaker (due to the influx of NaCl). These reaults also pointed to an underlying markedly unlinear dependence of hydrogen bonds energy on the NaCl concentration.

Table 6 represents the direct comparison of the Non-equilibrium Energy Spectra (NES) of the final solutions in the beaker and the ceramic cup after the occurrence of equilibrium at the end of the experiment.

The spectra are distinctly different in terms of positioning and magnitude of the local maxima. Unlike the solution in the beaker, the spectrum of the solution in the ceramic cup has nonzero values above for (–E) is (0.1087 eV) (λ = 11.41 μm) (ṽ = 877 cm^{-1}) and stronger expressed local maxima. Referring again to Table 5, it becomes clear that, even after reaching equilibrium, the average strength of hydrogen bonds in the ceramic cup is greater than that in the beaker. Consequently, even at equal NaCl concentrations, the hydrogen bonds energy distributions have been influenced by the previous history of osmosis and diffusion.

The IR absorption spectrum of NaCl aqueous solutions has a relatively characteristic peak at 1050 cm^{-1}. According to the above results for the NES of the physical solution (0.9 % NaCl) in the ceramic element at E = -0.1037 eV (λ = 11.96 μm; ṽ = 836 cm^{-1}), the hydrogen bonds energy distribution function value decreased from 50.2 to 0 eV^{-1}, while it increased from 0 to 60.3 eV^{-1} in the beaker.

It should also be pointed out that, in a study of several medicinal plants, a distinct common feature of their NES had been found [12 - 16]. In the deionized water control samples, the first non-zero values in the hydrogen bonds energy distribution appeared above E = -0.0937 eV (λ = 13.23 μm; ṽ = 756 cm^{-1}). In the experimental samples being 1.0 % v/v solutions of extracts from *Sideritis scardica* Griseb., *S. rosmarinu*s Spenn., *Tilia cordata* Mill., *Salvia divinorum* Epling. and *V. myrtillus* L., the first non-zero values in the corresponding distributions appeared above E = -0.1037 eV (λ = 11.96 μm; ṽ = 836 cm^{-1}), thus indicating greater hydrogen bonds strength. These results are similar to the findings in the present work being obtained through simultaneous osmosis and diffusion of physiological solution.

In addition, previous NES and IR Fourier analyses have identified spectral minima at E = -0.1037 (λ = 11.96 μm; ṽ = 836 cm^{-1}) and E = -0.1312 eV (λ = 9.45 μm; ṽ

= 1058 cm^{-1}) in sea water [17].

Additional research will be performed on sea and river waters for further elucidation of their energetic and informational characteristics. Practical results in power generation with nanopore barriers had already been achieved [18].

The presence of hydrogen ions (H^+) during diffusion in beaker allows us to assume that there is formation of hexagonal structures according to the formula $H^+(H_2O)_6$ [19].

CONCLUSIONS

Two solutions with equal NaCl concentrations were obtained by simultaneous osmosis and diffusion through a ceramic barrier. One of them started from 0.9 % and the other from 0 %, and reached equilibrium in 339 hours. Even though the process was relatively slow and the final solutions could be expected to have identical properties, distinct differences in their hydrogen bonds energy distributions were observed. Thus, hydrogen bond energies in this experiment were shown to be history-dependent. This result is of high significance for the future research on the water structure and its variability during physicochemical processes. In addition, interaction of water with ceramics, also in the presence of solutes, deserves further attention for fundamental and practical purposes. A key example in this regard could be the role of osmosis and diffusion in the origin of life. Moreover, changes in hydrogen bonds energy distributions of biological liquids passing through cell membranes could provide additional insights into the functioning of living matter.

REFERENCES

1. K. Sato, M. Ago, K. Ishikawa, T. Sato and K. Okajima, The structure of water induced by specific ceramics treatment and effects of treated water in view of some biological aspects, Environment Control in Biology, 43, 2005, 211-221.
2. T. Kozumi, Y. Kitagawa, Water structure changes induced by ceramics can be detected by increased permeability through aquaporin, Biochem. Biophys. Rep., 8, 2016, 5:353-358.
3. J. Kujawa, S. Al-Gharabli, G. Wrzeszcz, K. Knozowska, R. Lagzdins, E. Talik, A. Dziedzic, P. Loulergue, S. Patrick, A. Szymczyk and W. Kujawski, Physicochemical and magnetic properties of functionalized lanthanide oxides with enhanced hydrophobicity, Applied Surface Science, 542, 2021, 148563.
4. Bulgarian State Standard, Ceramic cylindrical filtering elements for chemical vessels and devices. Basic dimensions, BDS 7075.1968, 4.03.2022.
5. A. Antonov, Research of the non-equilibrium processes in the area in allocated systems. Dissertation thesis for degree Doctor of physical sciences, Blagoevgrad, Sofia, 1995, 1-254, (in Bulgarian).
6. S. Todorov, A. Damianova, I. Sivriev, A. Antonov, T. Galabova T. Water energy spectrum method and investigation of the variations of the H-bond structure of natural waters, Comptes Rendus de L'Academie Bulgare des Sciences, 61, 7, 2008, 857-862.
7. P. Gramtikov, A. Antonov, M. Gramatikova, A study of the properties and structure variations of water systems under the stimulus of outside influences, Fresenius Journal of Analytical Chemistry, 343, 1, 1992, 134-135.
8. I. Ignatov, G. Gluhchev, N. Neshev, D. Mehandjiev, Structuring of water clusters depending on the energy of hydrogen bonds in electrochemically activated waters anolyte and catholyte, Bulgarian Chemical Communications, 53, 2, 2021, 234-239.
9. D. Mehandjiev, I. Ignatov, N. Neshev, F. Huether, G. Gluhchev, Ch. Drossinakis, Formation of clusters in water and their distribution according to the number of water molecules, Bulgarian Chemical Communications, 54, 3, 2022, 211-216.
10. N. Neshev, I. Ignatov, R. Toshkova, Ch. Drossinakis, G. Gluhchev, Hydrogen bonds energy distribution and information-theoretic analysis of blood serum from hamsters with experimental Graffi tumor, Libri Oncologici, 50, 2-3, 2022, 52-61.
11. I. Ignatov, T. Popova, Applications of *Moringa oleifera* Lam., *Urtica dioica* L., *Malva sylvestris* L. and *Plantago major* L. Containing potassium for recovery, Plant Cell Biotechnology and Molecular Biology, 22, 7-8, 2021, 93-103.
12. I. Ignatov, T. P. Popova, R. Bankova, N. Neshev, Spectral analyses of fresh and dry Hypericum perforatum L. Effects with colloidal nano silver 30 ppm, Plant Science Today, 9, 1, 2022, 41-47.
13. I. Ignatov, V. Balabanski, M. Angelcheva, Application

of infrared spectral analyses for medicinal plants containing Calcium (Ca^{2+}), Plant Science Today, 9, 4, 2022.

14. I. Ignatov, F. Huether, N. Neshev, Y. Kiselova-Kaneva, T. P. Popova, R. Bankova, N. Valcheva, A. I. Ignatov, M. Angelcheva, I. Angushev, S. Baiti, Research of water molecules cluster structuring during *Haberlea rhodopensis* Friv. Hydration, Plants, 11, 19, 2022, 2655.
15. N. Neshev, I. Ignatov, Ch. Drossinakis, Measurement of hydrogen bond energies in some selected plants with medicinal properties and their information theoretical analysis, Plant Cell Biotechnology and Molecular Biology, 22, 45-46, 2021, 79-94.
16. I. Ignatov, N. Neshev, T. P. Popova, Y. Kiselova-Kaneva, Ch. Drossinakis, R. Bankova, R. Toshkova, G. Gluhchev, N. Valcheva, M. Angelcheva, G. Dinkov, I. Angushev, T. Todorova, V. Balabanski, S. Baiti, F. Huether, A.I. Ignatov, Theoretical analysis of hydrogen bonds, energy distribution and information in a 1 % Rosa damascena Mill oil solution, Plant Science Today, 9, 3, 2022, 760-765.
17. I. Ignatov, Origin of life and living matter in hot mineral water and properties of polar molecules in the primary hydrosphere and hydrothermal ponds, Uttar Pradesh Journal of Zoology, 42, 6, 2021, 37-52.
18. J. Feng, M. Graf, K. Liu, D. Ovchinnikov, D. Dumcenco, M. Heiranian, V. Nandigana, N. R. Aluru, A. Kis, Radenovic. Single-layer MoS_2 nanopores as nanopower generators. Nature, 536, 2016, 197–200.
19. T. H. Choi, K. D. Jordan, Application of the SCC-DFTB Method to $H^+(H_2O)_6$, $H^+(H_2O)_{21}$, and $H^+(H_2O)_{22}$, J. Phys. Chem. B, 114, 2010, 6932-6936.