

INFLUENCE OF THE CONTACT BETWEEN WATER AND A HYDROPHOBIC SURFACE ON SELF-DIFFUSION OF WATER MOLECULES

L.A. BULAVIN, A.A. VASYLKEVYCH¹, V.I. KOVALCHUK,
I.F. MYRONYUK², V.M. OGENKO³, V.I. SLISENKO¹, S.V. SYVOKIN

UDC 532.532

© 2005

Taras Shevchenko Kyiv National University
(6, Academician Glushkov Ave., Kyiv 03022, Ukraine),

¹**Institute for Nuclear Researches, Nat. Acad. Sci. of Ukraine**
(47, Nauky Ave., Kyiv 03028, Ukraine),

²**Institute of Chemistry of Surface (Pilot Plant), Nat. Acad. Sci. of Ukraine**
(Kalush 11-A8, Ivano-Frankivs'k Region 77300, Ukraine),

³**Institute of General and Inorganic Chemistry, Nat. Acad. Sci. of Ukraine**
(32/34, Academician Palladin Ave., Kyiv 03680, Ukraine)

Using the method of quasi-elastic scattering of slow neutrons, the influence of the contact between distilled water and a hydrophobic surface (porous silica covered with trimethylsilane $[-\text{Si}(\text{CH}_3)_3]_n$) on self-diffusion of water molecules has been studied. It has been established that after the contact of water with the hydrophobic surface the self-diffusion constant of water molecules increases due to the enhancing of the water collective motions, the latter being a result of water clusterization.

Water is considered nowadays as a three-dimensional polymeric net of molecules, where the weak intermolecular hydrogen bonds, in comparison with chemical ones, are in permanent reconstruction due to thermal fluctuations [1]. It has been found experimentally that if water contacts with a solid, the water molecules become ordered in a near-surface layer, thus forming quasi-dimensional structures [2–4].

When investigating the properties of water near the hydroxylated or trimethylsilanated surface of the pyrogenic silica (a silicagel) with the help of the nuclear magnetic resonance method, the authors of the work [4] revealed that the most perturbation influence on water occurs when the hydrophobic $[-\text{Si}(\text{CH}_3)_3]_n$ (trimethylsilane, TMS) coating is available on the SiO_2 surface (TMS– SiO_2). Moreover, the nano-sized particles of the trimethylsilanated silica demonstrate not only the absence of the phobic behavior at the contact with water but, on the contrary, stick to its surface and induce the polarization of water molecules in a layer of much greater thickness than that at the interaction with hydroxylated (hydrophilic) silica. It was suggested [5] that after the contact with a highly developed surface of the trimethylsilanated silica, the fragments of order are preserved in water, and the formed clusters do

not relax for a long time but persist even after the irradiation of water by ultrasound. For an explanation of the polarization origin of water molecules at the interface with a hydrophobic surface of the silica, the features of the electrostatic potential distribution near the surface of such disperse objects were elucidated [6]. A comparison of the corresponding profiles of the electrostatic potential distribution for the models of the hydroxylated and trimethylsilanated silica surfaces discovered an important specificity of this distribution in the latter case. In particular, the availability of the trimethylsilanated groups results in a formation on the surface of the SiO_2 nano-particles of the areas with a big positive electrostatic potential at large enough distances from the Si atoms [6]. At the same time, the influence of the solid surface on the molecular dynamics of water, which contacts with a solid, has not been studied at the microscopic level to date.

The aim of the work was to study the influence of a hydrophobic surface on the self-diffusion of the molecules of water, which is in a contact with this surface. Researches were carried out by the method of quasi-elastic scattering of slow neutrons [7] making use of a neutron spectrometer. A nuclear reactor BBP-M at the Institute for Nuclear Researches of the NAS of Ukraine was used as a source of neutrons.

It is of interest an opportunity to obtain such modified water, which contains clusters of the quasi-ordered structure, by means of its infiltration through a porous (granular) silica material made up of TMS– SiO_2 nano-particles [5]. In our work, TMS– SiO_2 in the form of grinded aerosil gel was used for the preparation of the specified water.

In the course of experiment, the energy spectrum of scattered neutrons was measured. An analysis of peak broadening in such spectra allows one to define the variations of the self-diffusion constant of water molecules in the specimens under investigation.

The block diagram of the experiment for the study of self-diffusion in water systems is shown in Fig. 1. A non-monochromatic beam of neutrons from reactor 1, formed by collimator 2, fell onto a crystal-monochromator 3 (a single crystal of zinc) at the angle ϕ with the reflection plane of the crystal. Due to the Bragg reflection at the angle 2ϕ with respect to the incident neutron beam, monochromatic neutrons with the energy of 13.2 meV were generated. With the help of the mechanical chopper 4, the steady beam of neutrons was converted into a pulsed one, which allowed the neutron spectrometry with respect to the time of the neutron flight to be carried out. The pulsed flux of neutrons arrived at a specimen in container 5. Eventual intensity variations of the monochromatic beam of neutrons were registered with the help of monitor 6. The neutrons scattered at various angles (namely, 9.5, 25.1, 40.5, 55.7, 70.9, 86.1, 101.3, and 116.5°) were registered by the system composed of eight detectors 7. The pulses from the registered neutrons were amplified by a preliminary amplifier 8 and through cathode-coupled amplifiers reached univibrators 9 operating as discriminators. The generated in such a manner pulses got to the inputs of corresponding time analyzers 10 (AI-4096), as well as to a computation block 11, which allowed the total number of pulses from each detector to be registered. The memory of the pulse time analyzers was split in accordance with the number of detectors into eight groups, each containing 25 time channels. Analyzers 10 were started with the help of differential amplifiers (DAs) and the magnetic head 12 of the mechanical chopper at the moment of the slit opening for the pulses of the neutron flux to pass.

The exposition time for each specimen was 21 h. at the temperature of 293 K. The intensity I_0 and the width ΔE of the quasi-elastic scattering peak were determined from the spectra obtained for each angle of scattering. The main body of information about the diffusive motions of the water molecules is contained exactly in the experimental dependence of the energy broadening ΔE of the quasi-elastic peak on the square of the transferred momentum q^2 (on the scattering angle) [7]. The analysis of those spectra, namely, the analysis of the quasi-elastic peak broadening, allows the self-diffusion constants of the water molecules to be determined.

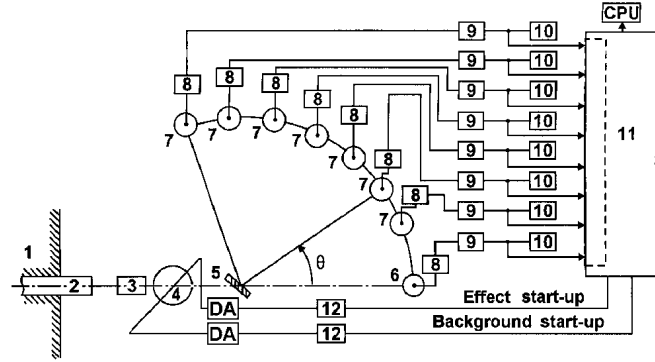


Fig. 1. Block diagram of the experimental setup for the study of self-diffusion in aqueous systems by the method of the quasi-elastic scattering of slow neutrons

The obtained experimental data concerning the measurement of the differential cross-section of the quasi-elastic scattering of slow neutrons in water before and after the contact with a hydrophobic surface can be analyzed in the framework of the existing models of diffusion. For the model of steady diffusion (a non-activation mechanism) [8]

$$\Delta E = 2\hbar q^2 D,$$

and for the model of step-like diffusion (an activation mechanism) [8]

$$\Delta E = \frac{2\hbar}{\tau_0} \left[1 - e^{-2W} (1 + q^2 D \tau_0)^{-1} \right],$$

where q is the momentum transfer of a neutron at the scattering, D is the diffusion constant of the liquid (water) molecules, W is the activation energy (the Debye–Waller factor), $\tau_0 \sim 10^{-12} \div 10^{-10}$ s is a characteristic parameter that means the average lifetime of hydrogen bonds.

Proceeding from the hierarchy of time scales of the fast one-particle and slow collective motions of water molecules in the Bulavin–Ivanov model [9], the broadening of the quasi-elastic peak can be represented as

$$\Delta E = \Delta E^{\text{op}} + \Delta E^{\text{col}}, \quad (1)$$

where ΔE^{op} and ΔE^{col} are the one-particle and collective contributions, respectively, into the broadening of the quasi-elastic peak. For the model of diffusion, which includes both the non-activation collective and activation one-particle modes of the water

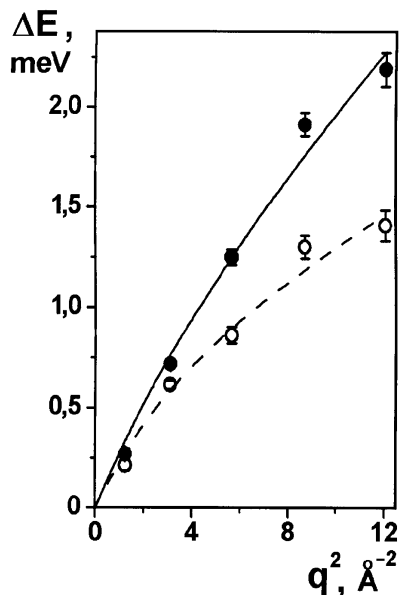


Fig. 2. Dependences of the quasi-elastic peak broadening ΔE on the square of the momentum transfer q^2 of the neutrons scattered at the molecules of distilled water before (the dashed curve) and after (the solid curve) the contact of water with a hydrophobic surface

molecule diffusion, the broadening of the quasi-elastic peak can be displayed in the form

$$\Delta E(q^2) = 2\hbar D^{\text{col}} q^2 + \frac{2\hbar}{\tau_0} \left[1 - \frac{\exp[-2W]}{1 + (D - D^{\text{col}}) q^2 \tau_0} \right], \quad (2)$$

where D^{col} is the collective contribution into the self-diffusion constant of H_2O molecules and $D^{\text{op}} = D - D^{\text{col}}$ is its one-particle counterpart.

At large values of the momentum transfer, $q \rightarrow \infty$, formula (2) transforms into the following one:

$$\Delta E(q^2) = 2\hbar D^{\text{col}} q^2 + 2\hbar \tau_0^{-1}, \quad (3)$$

which can be used for the determination of both the average lifetime of the hydrogen bond and the self-

Diffusion parameters obtained from the analysis of the experiment

| Specimen | $D \times 10^{-9}$, m^2/c | $D^{\text{col}} \times 10^{-9}$, m^2/c | $\tau_0 \times 10^{-2}$, c |
|---|---|--|--------------------------------|
| Distilled water | 1.13(±0.11) | 0.67(±0.32) | 1.91(±1.30) |
| Distilled water after the contact with a hydrophobic surface | 1.25(±0.09) | 0.86(±0.27) | 3.03(±2.79) |

diffusion constant D^{col} of water molecules in this medium:

$$D^{\text{col}} = \frac{1}{2\hbar} \frac{\partial \Delta E}{\partial (q^2)}. \quad (4)$$

The collective contribution to the diffusion constant is determined from the variation ΔE when the square of the transferred wave vector q^2 changes from 8 to 12.2 \AA^{-2} . Substituting the calculated in such a way values of D^{col} into formula (3), the value for τ_0 is obtained.

At small values of q , $q \rightarrow 0$, we obtain from formula (2)

$$\Delta E(q^2) = 2\hbar D q^2. \quad (5)$$

From here, we find

$$D = \frac{1}{2\hbar} \frac{\partial \Delta E}{\partial (q^2)}, \quad (6)$$

i.e. the total diffusion coefficient D is determined from the variation ΔE when q^2 changes from 0 to 1.5 \AA^{-2} .

Therefore, with the help of relations (4) and (6) concerning the peak broadening of the quasi-elastic neutron scattering, it is possible to calculate the diffusion coefficient of water molecules and the average lifetime of hydrogen bonds, and, thus, to draw a conclusion about the dynamics of water molecules before and after their contact with a hydrophobic surface. The results of such calculations are quoted in the Table.

In Fig. 2, the dependences of the quasi-elastic peak broadening ΔE on the square of the momentum transfer q^2 of the neutrons scattered at the molecules of distilled water before (the dashed curve) and after (the solid curve) the contact of the latter with a hydrophobic surface are depicted.

From the analysis of the experiment, it follows that the self-diffusion coefficient of water molecules increases (by about 10 %) after the contact of water with a hydrophobic surface. This growth of the self-diffusion coefficient occurs due to the enhancement of the contribution made by the collective motions of water molecules, which, in our opinion, is connected to the clusterization of water after its contact with a hydrophobic surface.

1. Antonchenko V.Ya. Physics of Water.— Kyiv: Naukova Dumka, 1986 (in Russian).
2. Spartakov A.A., Trusov A.A. // Kolloid. Zh.— 1998.— **60**, N 1.— P. 78—83.
3. Fesenko E.E., Terpuhov E.L. // Biofizika.— 1999. — **44**, N 1.— P.5—9.

4. *Turov V.V., Mironyuk I.F.* // Colloid. Surf. A.— 1998.— **134**.— P. 257 — 263.
5. *Mironyuk I.F.* // Dopovidi NANU.— 1999.— N 4. — P. 86 — 91.
6. *Mironyuk I.F., Lobaniv V.V., Ogenko V.M.* // Fiz. Khim. Tverd. Tila.— 2000.— **1**, N 2.— P. 177 — 184.
7. *Bulavin L.A.* Neutron Researches of Liquid Dynamics.— Kyiv: Vyshcha Shkola, 1977 (in Russian).
8. *Bulavin L.A.* Neutron Researches of Equilibrium and Transport Properties of Liquids: Thesis for Doctorate Degree in Physics and Mathematics.— Kyiv: T.G.Shevchenko Kyiv State Univ., 1989.
9. *Bulavin L.A., Verbinska G.M., Vyshnevskiy I.M.* Quasi-elastic neutron scattering in liquids.— Kyiv: ASMI, 2004.

Received 27.05.04.

Translated from Ukrainian by O.I.Voitenko

ВПЛИВ КОНТАКТУ З ГІДРОФОБНОЮ ПОВЕРХНЕЮ НА САМОДИФУЗІЮ МОЛЕКУЛ ВОДИ

*Л.А. Булавін, О.А. Василькевич, В.І. Ковальчук,
І.Ф. Миронюк, В.М. Огенко, В.І. Слісєнко,
С.В. Сивокинъ*

Резюме

Методом квазіпружного розсіяння повільних нейтронів досліджено вплив гідрофобної поверхні (пористий кремнезем, покритий триметилсиланом $[-Si(CH_3)_3]_n$) на самодифузію молекул дистильованої води, що перебуває в контакті з цією поверхнею. Встановлено, що після контакту води з гідрофобною поверхнею коефіцієнт самодифузії молекул води збільшується за рахунок зростання колективних рухів молекул води внаслідок її кластеризації.