# CONCENTRATION SPECIFIC FEATURES OF THE DYNAMICS OF MOLECULES IN SOLUTIONS WATER–PROPYL ALCOHOL

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By the method of quasielastic scattering of slow neutrons, we study the dynamics of molecules in water–propyl alcohol solutions of various concentrations at a temperature of 281 K. In experiments, we registered specific features of the concentration dependence of the efficient self-diffusion coefficient and its one-particle contribution, namely: the presence of two minima in the regions of (0.04÷0.05) mass fractions (m.f.) and (0.18÷0.22) m.f. of alcohol and a monotonous increase of the diffusion coefficient at concentrations greater than 0.4 m.f. of alcohol. The results of neutron-scattering experiments are compared with those of calculations of a structure of the mentioned solutions executed by the Monte-Carlo method. It is shown that the minima of the concentration dependence of the self-diffusion coefficient correspond to certain local structures of the solution under study.

Water is a specific fluid with regard for its chemicophysical properties. As known, these properties influence the behavior of water at its interaction with other substances. The water structure depends on the presence of hydrogen bonds which are formed due to a specific distribution of the charge density in a molecule. At the present time, there is no commonly accepted idea of the water structure, which does not allow one to describe all anomalous phenomena observed at the formation of water solutions (in particular, alcohol-water solutions) in a wide interval of thermodynamical parameters. Up to now, a great number of experiments on the study of properties of alcohol-water solutions as functions of their concentration and the temperature were carried out. Within the method of light scattering in water–alcohol solutions, the maximum of the integral scattering intensity was observed [1] at the content of alcohol $x \approx (0.15 \div 0.5)$ m.f. This maximum is named a normal peak. It is well described by the theory of light scattering by fluctuations of the concentration. In addition, one more peak, besides the normal one, was discovered at an alcohol concentration of (0.03÷0.05) m.f. in water–alcohol solutions [1]. To explain the anomalous behavior of water–alcohol solutions, we may use the model of microinhomogeneous cluster structure proposed in [2] for a glycerin – water system. The assumptions about the composition and the sizes of clusters which were made by the authors with the use of the stability condition for clusters are confirmed by estimates following from the thermodynamical calculations. As for water–alcohol solutions, their cluster structure at certain concentrations is corroborated by Monte-Carlo calculations performed for a water—ethyl alcohol solution [3, 4]. In this case, the concentration regions of solutions characterized by certain structural peculiarities are determined.

It is clear that the above-mentioned structural peculiarities of water–alcohol solutions must affect the dynamics of their molecules. Therefore, within the method of quasielastic scattering of slow neutrons (QSSN) [5], we have studied the self-diffusion of molecules in water–propyl alcohol solutions. As known, the QSSN method is especially sensitive to the dynamics of molecules in hydrogen-containing fluids and allows one to observe the diffusion motion of molecules during the time interval ($10^{-10} \div 10^{-12}$ s) and, thus, to obtain the information about the collective and one-particle motions of molecules.

The measurement of the quasielastic scattering spectra of slow neutrons was carried out on a many-detector time-of-flight spectrometer positioned at a VVR-M reactor at the Institute of Nuclear Research of the NAS of Ukraine in the scattering angle interval $25.1° \div 101.3°$. In experiments, we used monochromatic neutrons with an energy of 13.2 meV. We have studied the scattering of neutrons in water–propyl alcohol solutions in a wide

range of concentrations at a temperature of 281 K. In this case, we used thin specimens, in which the neutron flight length does not exceed 1 mm, which allowed us to neglect the corrections for the multiple scattering of neutrons. The obtained spectra of quasielastic scattering of neutrons with regard for the resolving power of a spectrometer were approximated by the Lorentz function

$$S(\mathbf{Q},\varepsilon) = \frac{\exp(-2W)\,2\hbar\,\Delta E(\mathbf{Q})}{\pi\left(\varepsilon^2 + \Delta E\,(\mathbf{Q})^2\right)} \qquad (1)$$

describing the quasielastic scattering of neutrons, $\exp\{-2W\}$ is the Debye–Waller factor, $\varepsilon = \hbar\omega$ is a change of the neutron energy at the scattering, $\mathbf{Q} = \mathbf{k} - \mathbf{k}_0$ is a change of the wave vector of a neutron in the process of scattering, and $\Delta E\,(\mathbf{Q})$ is a half-width of the quasielastic peak. By using the method of least squares, we approximated the quasielastic peak of scattered neutrons by function (1). As a result, we obtain the functional dependence $\Delta E\left(Q^2\right)$ containing the full information about the diffusion processes in the fluid system under study. In more details, the procedure of calculations is given in [5].

In the analysis of the dependences $\Delta E\left(Q^2\right)$ obtained on the basis of neutron spectra, we applied the Bulavin–Oskots'kyi–Ivanov model [6] which considers most completely the diffusion motions of molecules such as the oscillations of molecules around a center of temporary equilibrium, the hops of molecules from one center of equilibrium to another one (the so-called Frenkel mechanism of diffusion), and the diffusion of centers of equilibrium (the so-called Lagrange mechanism of diffusion). In the frame of this model, the widening of the peak is described by the formula

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

where $D$ is the total self-diffusion coefficient, $D_L$ is the coefficient of continuous (Lagrange) diffusion of the centers of oscillations of molecules, and $\tau_0$ is the duration of the settled life of a molecule in the position of equilibrium between two hops. In order to determine the parameters $D, D_L$, and $\tau_0$, the experimental dependences $\Delta E = \Delta E(Q^2)$ at a constant concentration of the solution were approximated by the theoretical curve (2) in the whole interval of variations of the square of the wave vector transferred.

The use of the conception of a hierarchy of the time scales of molecular motions [7] allows us to separate the self-diffusion coefficient $D$ into the collective (Lagrange) $D_L$ and one-particle (Frenkel) $D_F$ parts:

$$D = D_L + D_F. \qquad (3)$$

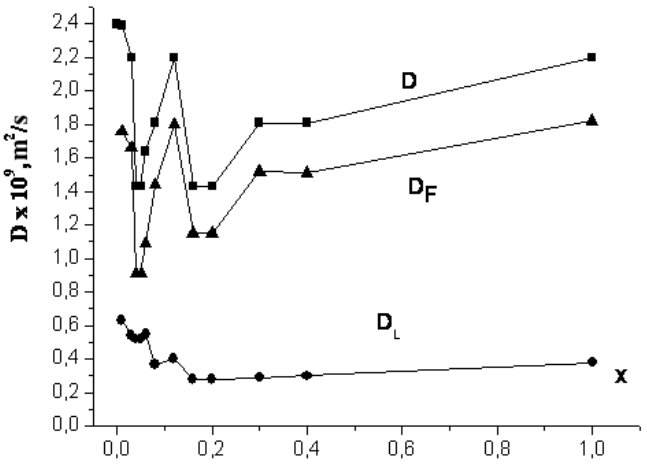


Fig. 1. Concentration dependence of the self-diffusion coefficient $D$, its collective $D_L$ and one-particle $D_F$ contributions. $X$ is the concentration of propyl alcohol in a water solution

The experimental concentration dependences of the self-diffusion coefficient $D$ and its components $D_L$ and $D_F$ are given in Fig. 1.

It is seen from Fig. 1 that the concentration dependences of the effective self-diffusion coefficient $D$ of molecules of a propanol–water solution and its one-particle component $D_F$ have two minima, respectively, at the concentrations of alcohol $x = (0.04 \div 0.05)$ m.f. and $x = (0.18 \div 0.22)$ m.f., which testifies to a significant deceleration of diffusion motions and a decrease in the one-particle contribution at the indicated concentrations. The minimum at a higher concentration of alcohol has a greater width and corresponds to the scattering of neutrons by fluctuations of the concentration.

It is worth noting that the scattering cross-section of slow neutrons by hydrogen atoms is more approximately by a factor of 20 than those by the other atoms. This implies that neutrons "feel" mainly the motions of hydrogen atoms in molecules of alcohol and water containing hydrogen and, therefore, give information about the fluid dynamics only to that extent, at which this dynamics is reflected in motions of these atoms. At a concentration of 0.04 m.f. of propyl alcohol in water, the ratio of protons in alcohol molecules and water molecules amounts to 1:6. Hence, neutrons reflect mainly the dynamics of water molecules in a solution. But, at a concentration of 0.2 m.f. of alcohol, the numbers of protons in molecules of alcohol and water are

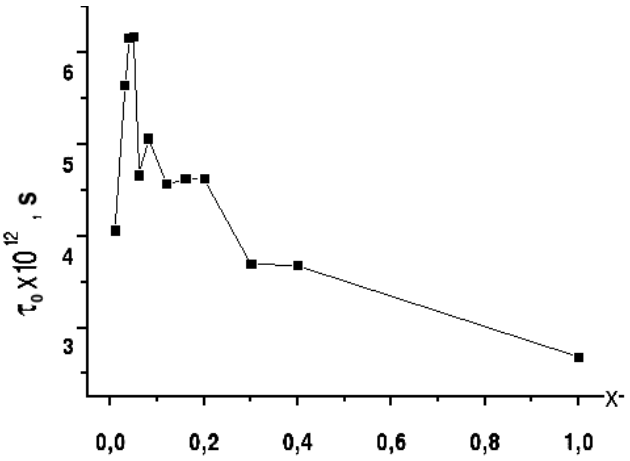


Fig. 2. Dependence of the duration of the settled life of molecules in the position of equilibrium on the concentration of alcohol in water–propanol solutions

the same. In this case, the contributions to the widening of the quasielastic peak from motions of molecules of alcohol and water are almost identical. In the interval of concentrations $x = (0.18 \div 0.22)$ m.f. of alcohol, the collective component $D_L$ of the self-diffusion coefficient attains a minimum value and then monotonically increases. The monotonous increase of the total self-diffusion coefficient and its components is characteristic at concentrations more than 0.4 m.f. of alcohol.

Based on the experimental data on the quasielastic scattering of slow neutrons and relation (2), we made attempt to evaluate the mean duration of the stay of molecules in the position of equilibrium. As seen from Fig. 2, the concentration dependence of the duration of the settled life of molecules $\tau_0$ in the position of equilibrium has a maximum in the alcohol concentration region $x = (0.04 \div 0.05)$ m.f. and a wide maximum in the region of concentrations $x = (0.18 \div 0.22)$ m.f. of alcohol. Such significant increase in the duration of the settled life indicates a local structural reconstruction of solutions at the indicated concentrations, and the widths of maxima demonstrates the fundamental difference of mechanisms of these processes for two given concentrations.

A significant deceleration of diffusion motions and an increase in the duration of the settled life in the indicated region of concentrations (Figs. 1 and 2) are related, in our opinion, to the formation of stable water–alcohol complexes.

Such a behavior of the self-diffusion coefficient and the duration of the settled life at a change of the solution concentration become understandable if we compare the results of neutron experiments to those obtained by us within the Monte-Carlo method for the structure of water — propyl alcohol solutions. As a result of the computer simulation, we obtained the dependences of the mean energies of components of the intermolecular interaction (the interaction between water molecules, the interaction between molecules of alcohol, and the interaction between water molecules and alcohol), the radial distribution functions, and the numbers of the nearest neighbors. On the basis of the data obtained, we have determined the regions, where the local structure of a solution varies, and propose the model ideas for the description of a structure of the water–propyl alcohol system under study at various concentrations.

According to the calculations, we can separate several regions of concentrations of water–alcohol solutions with a local structure characteristic of each region.

### *1. Concentration of Propyl Alcohol in a Water Solution with $x < 0.04$ m.f.*

The introduction of propanol molecules into water in this region of concentrations does not lead to breaks in the network of hydrogen bonds which is formed by water molecules. A propanol molecule introduced into a solution is surrounded by $(7 \div 8)$ water molecules, and the interaction between molecules of propanol at large distances does not cause the formation of complexes with molecules of alcohol. In this region of concentrations, the water clusters are composed of 6 molecules of water. In this case, the self-diffusion coefficient of water molecules in the alcohol solution is close to the self-diffusion coefficient of pure water.

### *2. Concentration of Propyl Alcohol in a Water Solution with $x \sim (0.04 \div 0.1)$ m.f.*

In the limits of this region of concentrations, there occurs a reconstruction of water clusters and a decrease in the number of molecules in them to five. Complexes which are composed of at least one water molecule and one propanol molecule are formed. At the same time, there exist the systems including one propanol molecule surrounded by $(7 \div 8)$ water molecules.

The formation of complexes of water molecules and alcohol leads to a significant deceleration of the diffusion motion and an increase in the duration of a settled life of water molecules in a position of equilibrium. This explains the presence of the minimum in

the concentration dependence of the self-diffusion coefficient $D$ and its one-particle contribution $D_F$, as well as the presence of the maximum of $\tau_0$ at concentrations $x = (0.04 \div 0.05)$ m.f., which was observed in the neutron experiments.

### *3. Concentration of Propyl Alcohol in a Water Solution with $x \sim (0.1 \div 0.25)$ m.f.*

In the region of concentrations $x \sim (0.1 \div 0.18)$ m.f., there occurs the further reconstruction of water clusters and a decrease in the number of their molecules to four. As a result, the systems composed of two water molecules and, as a minimum, one propanol molecule are formed. In addition, we assume the presence of systems including a single water molecule and one propanol molecule, as well as systems of $(7 \div 8)$ water molecules surrounding a single propanol molecule.

As a concentration $x \sim (0.18 \div 0.22)$ m.f. is attained, we can assume the formation of clusters of six propanol molecules surrounded by (18-20) water molecules due to the hydrophobic interaction of propanol molecules between themselves and the interaction between molecules of water and propanol. In the limits of concentrations $x \sim (0.18 \div 0.25)$ m.f., the systems composed of water molecules surrounding one propanol molecule continue to exist. These systems are analogous to those which are registered in infinitely diluted solutions.

In the region of concentrations $x \sim (0.18 \div 0.22)$ m.f. of alcohol, the data of neutron experiments on the concentration dependence of the coefficient self-diffusion $D$ and its one-particle component $D_F$ indicate the presence of the second wider minimum and maximum of the concentration dependence $\tau_0$.

### *4. Concentration of Propyl Alcohol in a Water Solution with $x \sim (0.25 \div 0.4)$ m.f.*

In the limits of this region of concentrations, there occurs the formation of a structure of clusters of propanol molecules. Near concentrations greater than $x \sim 0.3$ m.f., these clusters include four propanol molecules surrounded by eight water molecules. In this case, two water molecules are present in the vicinity of an alkyl chain of propanol molecules, and a single water molecule is near the hydroxyl group of a propanol molecule.

We note that, at the concentration of alcohol $x \geq 0.3$ m.f., the structure of clusters of propanol molecules reminds that of micellae. The interior and exterior of clusters contain, respectively, hydroxyl groups and alkyl groups of propanol molecules.

### *5. Concentration of Propyl Alcohol in a Water Solution with $x > 0.4$ m.f.*

In this region of the concentration, we observe a monotonous increase in the self-diffusion coefficient and its components, as well as a monotonous decrease in the duration of the settled life, as the concentration of alcohol in water increases. The increase in the collective contribution to the self-diffusion coefficient testifies that the solutions contain the centers of oscillations surrounded by hydration shells. As the centers of oscillations, we may consider the micella-like complexes formed by molecules of alcohol surrounded by the first and second hydration shells. At the same time, the increase in the one-particle component of the self-diffusion coefficient with the concentration of alcohol in a solution indicates the presence of free water molecules in solutions or temporarily liberated water molecules which appear during their transfer from one hydration shell to another one. Free molecules of alcohol not bound in complexes can also exist.

The increase in the self-diffusion coefficient and the decrease in the duration of the settled life of molecules in a position of equilibrium at a further increase in the concentration of alcohol are a consequence of the decrease in the number of water molecules in hydration shells, which causes an increase in the mobility of propanol molecules.

Thus, within the method of the quasielastic scattering slow of slow neutrons and the method of Monte-Carlo, we have studied the influence of the concentration of alcohol on a local and energy properties of the water–propanol system. The analysis of the obtained radial distribution functions in these liquid systems allowed us to separate several regions of concentrations of the water–alcohol solution with a local structure of a solution characteristic of each region. The existence of the separated regions of concentrations in the water—propyl alcohol system is confirmed experimentally by the method of quasielastic scattering of slow neutrons. We have revealed the minima on the concentration dependences of the self-diffusion coefficient $D$ and its one-particle component $D_F$ at the concentrations $x = (0.040 \div 0.05)$ m.f. and $x = (0.18 \div 0.22)$ m.f. of alcohol which correspond to certain local structures of a solution.

1. M.F. Vuks, *Scattering of Light in Gases, Fluids, and Solutions* (Leningrad State Univ., Leningrad, 1977) (in Russian).

2. V.E. Chechko, T.V. Lokotosh, M.P. Malomuzh *et al.*, Zh. Fiz. Dosl. **7**, 175 (2003).

3. N.A. Atamas, A.A. Atamas, and L.A. Bulavin, Russian J. Phys. Chem. **78**, 1080 (2004).

4. N.A. Atamas and A.A. Atamas, Proceed. of World Academy of Sci., Eng. and Techn. **55**, 1 (2009).

5. L.A. Bulavin, G.M. Verbins'ka, and I.M. Vyshnevs'kyi, *Quasielastic Scattering of Slow Neutrons in Fluids* (ASMI, Poltava, 2004) (in Ukrainian).

6. L.A. Bulavin, G.N. Verbinskaya, and V.T. Krotenko, Fiz. Zhidk. Sost. **19**, 40 (1991).

7. L.A. Bulavin, A.A. Vasilkevich, A.K. Dorosh *et al.*, Ukr. Fiz. Zh. **31**, 1703 (1986).

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КОНЦЕНТРАЦІЙНІ ОСОБЛИВОСТІ ДИНАМІКИ МОЛЕКУЛ РОЗЧИНІВ ВОДА—ПРОПИЛОВИЙ СПИРТ

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Р е з ю м е

Методом квазіпружного розсіяння повільних нейтронів проведено дослідження динаміки молекул розчинів вода–пропиловий спирт різної концентрації при температурі 281 K. Експериментально виявлено особливості концентраційної залежності ефективного коефіцієнта самодифузії та його одночастинкового внеску, а саме: наявність двох мінімумів в областях концентрацій (0,04–0,05) м.д. і (0,18–0,22) м.д. спирту та монотонне зростання коефіцієнта дифузії при концентраціях, більших за 0,4 м.д. спирту. Результати нейтронного експерименту зіставлено з розрахунками структури указаних розчинів, проведених методом Монте-Карло. Показано, що мінімуми у концентраційній залежності коефіцієнта самодифузії відповідають певним локальним структурам дослідженого розчину.