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## **Self-diffusion of molecules in water-ethanol solutions of low concentration. Neutron data**

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*The work is devoted to the abnormal behavior of dilute water-alcohol solutions. The dynamics of molecules of the water-ethanol system, depending on the concentration at 281 K, is researched by the method of quasi-elastic scattering of slow neutrons. The total self-diffusion coefficient of molecules  $D$ , its single-particle  $D_{s-p}$  and collective  $D_{coll}$  components, and the time of settled molecule's life in the oscillating state  $\tau_0$  are determined. The region of small concentrations was studied in detail, and two minima in the coefficients  $D$  and  $D_{s-p}$  were detected in the vicinity of concentrations  $X=0.04$  mol.f. and  $X=0.2$  mol.f. Time  $\tau_0$  at these concentrations is increasing significantly. This indicates a significant decrease in the intensity of the activation mechanism of diffusion of molecules, which is quite possible due to the binding of water and ethanol molecules into complexes (clusters).*

**Keywords:** *quasi-elastic scattering of slow neutrons, self-diffusion coefficient, single-particle and collective components of the self-diffusion coefficient, cluster, ethanol, dilute aqueous-alcohol solutions.*

It is known that water-alcohol solutions (isopropanol, propanol, tertiary butanol, glycerol, etc.) are characterized by an abnormal behavior at low concentrations of 0.03–0.5 molar fractions (mol.f.) of alcohol [1]. An abnormal molecular light scattering (MLS) was found long time ago at a concentration of 0.2–0.5 mol.f. (normal peak) and at ~0.05 mol.f. (abnormal peak) of the integral intensity of MLS. The normal peak is well described by the quasithermodynamic theory of fluctuations [2]. The abnormal peak has several features that are absent in the normal peak. It is observed in dilute solutions of most alcohols at the same concentration ~0.045 mol.f. Its half-width is much smaller than the half-width of the normal peak, and the amplitude increases with a decrease of the temperature [3]. This behavior of these two peaks indicates their different nature.

There are several approaches to explaining the unusual properties of a dilute water-alcohol solution. According to one of them, near a special point ( $X = 0.045$  mol.f.), this solution is thermodynamically unstable and decomposes into two states, which leads to the appearance of nuclei with a new structure [4]. In the work [5], it was shown that the abnormal MLS is caused by in-

tense clusterization processes near a special point. Diluted water-alcohol solutions can be considered as a solution of stable clusters, which consist of two-three alcohol molecules and about ten water molecules. It is obvious that the appearance of a new structure or the formation of clusters in the vicinity of a special point will affect the dynamics of molecules of a water-alcohol solution. Therefore, the purpose of this work was to identify the impact on the dynamic processes of changing the concentration of alcohol in the water-alcohol system at the special point. In addition, as for the dilute aqueous solutions of ethanol, the controversial information is still present. So, according to [6], the anomalous peak in MLS of these solutions is absent in general, and, according to [7], it is observed even at 0.09 mol.f.

**The method of quasi-elastic scattering of slow neutrons.** Different experimental methods are available for studying different molecular processes, depending on their specific times. In particular, the method of quasi-elastic scattering of slow neutrons is very effective in studying the dynamics of the condensed state of a substance. It is based on the interaction of neutrons with diffusion movements of particles (atoms, molecules) and allows one to obtain information about them in the time interval ( $10^{-11}$ – $10^{-12}$  s). The complex nature of the particle motion in a liquid complicates the description of neutrons scattered by them. The presence of the diffusion (individual) motion of particles in a fluid, in addition to the collective movements inherent in the solids, leads to the appearance of a quasi-elastic component in the neutron spectrum, which manifests itself as an extension of the monochromatic neutron line.

To interpret the quasi-elastic neutron scattering (QENS) by fluids, the method of space-time functions is used, which allows the double-differential neutron cross-section to be associated with the function of the pair space-time correlations of particles that scatter.

The double differential neutron scattering cross-section on a system of  $N$  particles within the framework of Van Hove's formalism [8, 9] has the form

$$\frac{d\sigma}{d\Omega d\varepsilon} = N\sigma_{\text{inc}} \frac{k}{\hbar k_0} S(\vec{Q}, \varepsilon), \quad (1)$$

where  $\sigma_{\text{inc}}$  – is the cross-section of incoherent neutrons scattering;  $\vec{k}_0, \vec{k}$  – the wave vector of the incident and scattered neutrons, accordingly;  $\vec{Q} = \vec{k}_0 - \vec{k}$  – change of neutron pulse at its scattering;  $\varepsilon = \hbar\omega$  – change of the neutron energy at the process of scattering;  $S(\vec{Q}, \varepsilon)$  – law of neutron scattering.

Expression (1) was obtained for incoherently scattering substances, which, in particular, are hydrogen-containing fluids. Since the incoherent component of the neutron scattering cross-section on protons is about 10 times greater than the scattering cross-sections of nuclei of other atoms, this leads to the fact that the dynamics of molecules of hydrogen-containing fluids is investigated by the neutron method indirectly – through the diffusion motion of hydrogen atoms.

To simplify the description of QENS on liquids, there were created several models of the self-diffusion process. In this work, we used the model outlined in [10–12], in which the following diffuse motions of a fluid molecule are considered when calculating the scattering law: the molecule oscillates near the center of temporary equilibrium for a time of  $\tau_0$ ; jumps of the molecule during time  $\tau_1$  from one equilibrium center to another one (activation mechanism of diffusion); movement (diffusion) of equilibrium centers. We also take the rotating motion of diffuse particle into account. In the case of quasicrystalline fluids such as water and its solutions,

the condition  $\tau_0 \gg \tau_1$  is fulfilled, and the law of neutron scattering in (1) is written as the Lorentz function [10–12]

$$S(Q, \varepsilon) = \frac{1}{\pi} e^{-2W} \frac{\Delta E}{\varepsilon^2 + (\Delta E)^2} \quad (2)$$

with the half-width

$$\Delta E = 2\hbar D_{\text{coll}} Q^2 + \frac{2\hbar}{\tau_0} \left[ 1 - \frac{e^{-2W}}{1 + Q^2 (D - D_{\text{coll}}) \tau_0} \right], \quad (3)$$

where  $D$  – total self-diffusion coefficient;  $e^{-2W}$  – Debye–Waller factor.

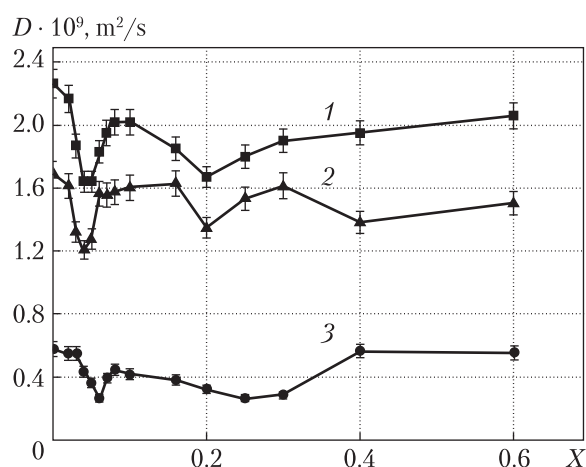
In [13], it was proposed to divide the total self-diffusion coefficient  $D$  into two components: a single-particle (s-p)  $D_{\text{s-p}}$  and a collective  $D_{\text{coll}}$ , based on the hierarchy of the time scales of molecular movements – fast single-particle and slow collective movements, which manifest themselves at small and long observation times of a diffusing particle. In the neutron experiment, this time is associated with the transmitted pulse as follows:

$$\frac{1}{2DQ^2}. \quad (4)$$

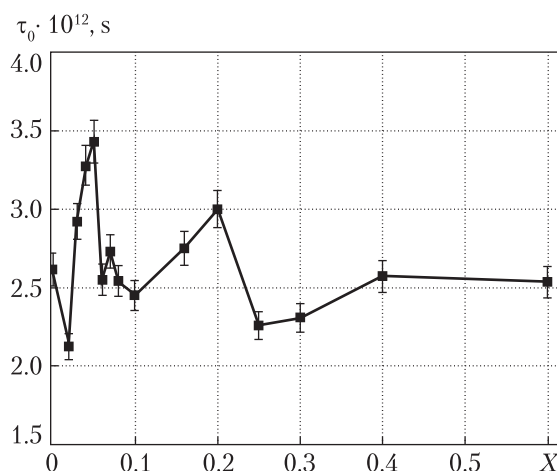
So, large observation times are realized for small  $\bar{Q}$  and, accordingly, small for large  $\bar{Q}$ . The neutron spectrometer, which was used in these studies, allows one to measure the spectrum of QENS in the range of transmitted pulses of  $1.09 \text{ nm}^{-1} \leq Q \leq 3.42 \text{ nm}^{-1}$ . At the edges of this interval, the time  $t$  is accordingly equal to  $\sim 10^{-11}$  and  $\sim 10^{-12}$  s, which allows information to be obtained only for slow collective movements or only for the rapid individual movements of diffusing particles. The total coefficient of self-diffusion in this case can be written as the sum of contributions of these components of the self-diffusion [13]:

$$D = D_{\text{coll}} + D_{\text{s-p}}. \quad (5)$$

**Experimental part.** The experiments were carried out on a multidetector neutron time-of-flight spectrometer located at the research reactor WWR-M of the Institute for Nuclear Research of the NAS of Ukraine. The neutron spectra were measured in the range of scattering angles of  $25.1^\circ - 86.1^\circ$ . Monochromatic neutrons with an energy of 13.2 meV were used in experiments. The neutron scattering in water-ethanol solutions was investigated within the concentrations of 0.02–0.6 mol.f. at a temperature of 281 K. The studied samples were in a 0.9 mm thick container. The proportion of neutrons scattered in those samples does not exceed 20 % of their total number, which allowed the corrections for multiple neutron scattering to be neglected. Each neutron spectrum represents a superposition of inelastic and quasi-elastic neutron scatterings that does not have a clear boundary. Therefore, there is a problem of separating the quasi-elastic component from the neutron spectrum, which, as noted above, is caused by the diffusion motion of the solution molecules. The procedure for such separation is described in detail in [14]. The quasi-elastic spectra obtained with regard for the resolution function of a spectrometer were approximated by Lorentzian (2). In the process of adjusting spectrum (2) to the experimental one, by the least squares method, the half-widths  $\Delta E$  of all the QENS spectra were determined, and the function



**Fig. 1.** Concentration dependence of the total self-diffusion coefficient  $D$  (1) and its single-particle  $D_{s-p}$  (2) and collective  $D_{coll}$  (3) components of a water-ethanol solution



**Fig. 2.** Concentration dependence of the lifetime of a molecule in the oscillating state in a water-ethanol solution

nal dependence  $\Delta E(Q^2)$  which contains information about the diffusion processes in a fluid, is obtained. To analyze the  $\Delta E(Q^2)$  dependences obtained on the basis of neutron spectra, as already noted above, we used a model in [10–12]. The concentration dependence of the total self-diffusion coefficient and its components obtained in this way is presented in Fig. 1, and the settled life time of a molecule is shown in Fig. 2.

**Research results and their discussion.** From Fig. 1, we can see that, first of all, the total self-diffusion coefficient  $D$  remains less than the self-diffusion coefficient of  $D_W$  of pure water in the whole range of studied concentrations. Only as  $X \rightarrow 0$ , it is approaching  $D_W$ . Second, the main contribution ( $\sim 75\%$ ) to the total self-diffusion coefficient  $D$  of a water-ethanol solution belongs to its single-particle  $D_{s-p}$  component. Third, the features inherent to the coefficient  $D_{s-p}(X)$  are also observed in the coefficient  $D(X)$ . These are two minima at the concentrations  $X = 0.04$  mol.f. and  $X = 0.2$  mol.f. At the same time, the settled life of a molecule in the oscillating state  $\tau_0$  (see Fig. 2) increases significantly, which is visible in the form of two maxima. Therefore, there is a significant decrease in the diffusion intensity by the activation mechanism at these concentrations. The first minimum in  $D(X)$  and  $D_{s-p}(X)$  in comparison with the second one has a smaller width and a greater amplitude, which is quite possible due to the different nature of the processes that determine them.

In Fig. 1, we show the collective component  $D_{coll}(X)$  of the total self-diffusion coefficient, in which, as we see, there are also two minima, but a much less amplitude. In addition, they are shifted toward higher concentrations. The first minimum is located at 0.06 mol.f., and the second at  $\sim 0.25$  mol.f. Moreover, it is much wider than the first minimum.

In [5], considering the aqueous solutions of glycerin, it was assumed that the abnormal properties of dilute aqueous solutions of alcohols are caused by the appearance of strong hydrogen bonds between molecules of water and alcohol, which is accompanied by the intensive formation of clusters. An elementary cluster consists of two or three molecules of alcohol and ten molecules of water and has a size  $\sim 6$  Å. It is stable and is proposed to be regarded as a pseudoparticle [5].

It should be noted that, at a concentration of 0.04 mol.f. of alcohol, the ratio of protons in alcohol molecules and water molecules is 1 : 8. It would seem that the scattered neutrons in this case give information, mainly, about the diffusion movements of water molecules. However, in the cluster, this ratio is already  $\sim 1 : 4$ , and the contribution of QENS to proton molecules of alcohol significantly increases. As a result, we obtain the averaged values of the parameters of the diffusion of alcohol molecules and water molecules. This refers to the components of the  $D_{s-p}$  of the total self-diffusion coefficient.

On the one hand, the emergence of clusters leads to an increase in the number of water molecules with greater binding energy (in a cluster). On the other hand, the process of solution clustering leads to decreasing the number of molecules in the free volume of the solution. Both of these factors cause the decrease of the intensity of the activation mechanism in the water molecule diffusion and therefore reduce the single-particle component  $D_{s-p}$  of the full self-diffusion coefficient  $D$ , which manifests itself as a minimum at a concentration of 0.04 mol.f. (see Fig. 1).

In conclusion, we note the following: with the help of the QENS method in the concentration dependence of the total coefficient of self-diffusion  $D$  and its one-particle component  $D_{s-p}$  of dilute water-ethanol solutions, a number of features were revealed. However, in our case, the position of the special point (0.04 mol.f.) does not match with the data on the light scattering, according to which the abnormal peak is located at 0.09 mol.f. [7].

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#### САМОДИФУЗИЯ МОЛЕКУЛ У РОЗЧИНАХ ВОДА—ЕТАНОЛ МАЛОЇ КОНЦЕНТРАЦІЇ. НЕЙТРОННІ ДАНІ

Розглянуто аномальну поведінку розбавлених водно-спиртових розчинів. Методом квазіпружного розсіяння повільних нейтронів досліджено динаміку молекул системи вода—етанол залежно від концентрації при температурі 281 К. Визначені загальний коефіцієнт самодифузії молекул  $D$ , його одночастинкова  $D_{s-p}$  і колективна  $D_{coll}$  складові та час осілого життя молекули в коливному стані  $\tau_0$ . Детально вивчено область малих концентрацій, де в околі концентрацій  $X = 0,04$  мол.ч. і  $X = 0,2$  мол.ч. у коефіцієнтах  $D$  та  $D_{s-p}$  виявлено два мінімуми. Час  $\tau_0$  при цих концентраціях істотно зростає. Це вказує на значне зменшення при даних концентраціях інтенсивності активаційного механізму дифузії молекул, що, цілком можливо, зумовлено зв'язуванням молекул води та етанолу в комплекси (кластери).

**Ключові слова:** *квазіпружне розсіяння повільних нейтронів, коефіцієнт самодифузії, одночастинкова і колективна складові коефіцієнта самодифузії, кластер, етанол, розбавлені водно-спиртові розчини.*

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#### САМОДИФУЗИЯ МОЛЕКУЛ В РАСТВОРАХ ВОДА—ЭТАНОЛ МАЛОЙ КОНЦЕНТРАЦИИ. НЕЙТРОННЫЕ ДАННЫЕ

Рассмотрено аномальное поведение разбавленных водно-спиртовых растворов. Методом квазиупругого рассеяния медленных нейтронов исследована динамика молекул системы вода—этанол в зависимости от концентрации при температуре 281 К. Определены общий коэффициент самодиффузии молекул  $D$ , его одночастичная  $D_{s-p}$  и коллективная  $D_{coll}$  составляющие и время оседлой жизни молекулы в колебательном состоянии  $\tau_0$ . Подробно изучена область малых концентраций, где в окрестности концентраций  $X = 0,04$  мол.д. и  $X = 0,2$  мол.д. в коэффициентах  $D$  и  $D_{s-p}$  обнаружено два минимума. Время  $\tau_0$  при этих концентрациях существенно возрастает. Это указывает на значительное уменьшение при данных концентрациях интенсивности активационного механизма диффузии молекул, что, вполне возможно, обусловлено связыванием молекул воды и этанола в комплексы (кластеры).

**Ключевые слова:** *квазиупругое рассеяние медленных нейтронов, коэффициент самодиффузии, одночастичная и коллективная составляющие коэффициента самодиффузии, кластер, этанол, разбавленные водно-спиртовые растворы.*