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**NEUTRON STUDIES OF DIFFUSION PROCESSES NEAR A SINGULAR POINT
IN A DILUTE AQUEOUS SOLUTION OF ETHANOL**

The problem considered in this work relates to the physics of liquids. Rather, to the physics of dynamic processes in liquids. The method of quasielastic scattering of slow neutrons was used to study the dynamics of molecules of the water-ethanol system as a function of concentration at a temperature of 8 °C and as a function of temperature at a concentration of $X = 0.04$ molar particles (mol. particl.). The overall coefficient of self-diffusion of molecules D , its single-particle D_{s-p} and collective D_{coll} components, as well as the time of settled life of a molecule in a vibrational state τ , are determined. The region of small concentrations was studied in detail, where in the vicinity of concentrations $X = 0.04$ mol. particl. and $X = 0.2$ mol. particl. two minima are found in the coefficients D and D_{s-p} . Time τ at these concentrations increases significantly. This indicates a significant decrease in the intensity of the activation mechanism of molecular diffusion at these concentrations, which is quite possibly caused by the binding of water and ethanol molecules into complexes (clusters). Similarly, a deep minimum was found in the D and D_{s-p} coefficients near the temperature of 4 °C. Time τ at this temperature also increases. That is, at a temperature of 4 °C, the intensity of the activation mechanism of the diffusion of solution molecules decreases. Therefore, at a concentration of $X = 0.04$ mol. particl. and at a temperature of 4 °C, a special point exists in the water-ethanol system. However, its position does not coincide with the data on scattering light.

Keywords: quasielastic scattering of slow neutrons, self-diffusion coefficient, single-particle and collective components of the self-diffusion coefficient, cluster, ethanol, diluted water-alcohol solutions.

1. Introduction

It is known that water-alcohol solutions (isopropanol, propanol, tertiary butanol, glycerol, etc.) are characterized by abnormal behavior at low concentrations of 0.03 - 0.5 molar particles (mol. particl.) of alcohol [1]. An abnormal molecular light scattering (MLS) was found a long time ago at a concentration of 0.2 - 0.5 mol. particl. (normal peak) and at ~0.05 mol. particl. (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. particl. Its half-width is much smaller than the half-width of the normal peak, and the amplitude increases with a decrease in the temperature [3]. The 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. particl.), 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 intense 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 of the dynamic processes of changing temperature and the concentration of alcohol in the water-alcohol system at the special point. In addition, as for the dilute aqueous solutions of ethanol, 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. particl.

**2. Method of quasielastic scattering
of slow neutrons**

Different experimental methods are available for studying different molecular processes, depending on their specific times. In particular, the method of quasielastic 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 quasielastic component in the neutron spectrum, which manifests itself as an extension of the monochromatic neutron line.

To interpret the quasielastic neutron scattering (QENS) by fluids, the method of spacetime 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

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

where σ_{HK} – 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 in its scattering; $\varepsilon = \hbar\omega$ – change of neutron energy at the process of scattering; $S(\vec{Q}, \varepsilon)$ – law of the 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 fluids, 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 τ_0 ; jumps of the molecule during time τ_1 from one equilibrium center to another one (activation mechanism of diffusion); movement (diffusion) of equilibrium centers. We also consider the rotating motion of diffuse particles. 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:

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

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_{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 \vec{Q} and, accordingly small for large \vec{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 $1.1 \cdot 10^{-2} \text{ nm}^{-1} \leq Q \leq 3.4 \cdot 10^{-2} \text{ nm}^{-1}$. 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 self-diffusion [13]:

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

3. Experimental part

The experiments were carried out on a multidetector neutron time-off light 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 $25.1^\circ - 86.1^\circ$. The energy resolution of the spectrometer (the half-width of the elastic scattering of neutrons on vanadium) was equal to $\Delta E_0 \approx 0.7 \text{ meV}$. Monochromatic neutrons with an energy of 13.2 meV were used in experiments. The research was conducted in two directions. First, the scattering of neutrons in water-ethanol solutions within the concentration range of $0.02 - 0.6 \text{ mol. particl.}$ was investigated often at a temperature of 8°C . And, secondly, diffusion processes in this solution were studied at a concentration of $0.04 \text{ mol. particl.}$ in the temperature range of 1.5°C

- 8 °C. The studied samples were in 0.9 mm thick containers. The proportion of neutrons scattered in this sample does not exceed 20 % of their total number, which allowed the corrections for multiple neutron scattering to be neglected. In the temperature experiments, the container with the sample was placed in a special thermostat based on Peltier elements. The temperature was maintained with an accuracy of ± 0.1 °C. Each neutron spectrum represents a superposition of inelastic and QENS that does not have a clear boundary. Therefore, there is a problem with separating the quasielastic 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

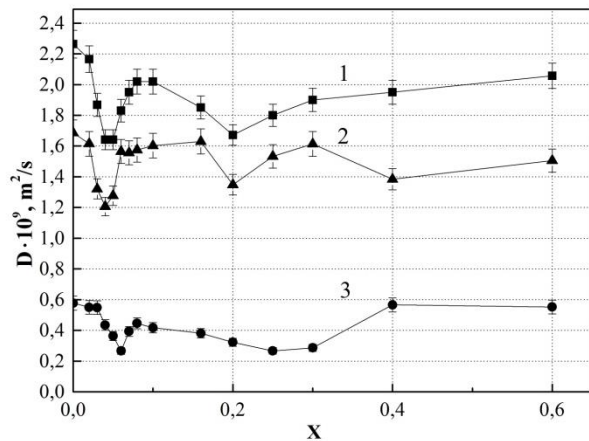


Fig. 1. Concentration dependence of the total self-diffusion coefficient D (1) and its single-particle D_{sp} (2) and collective D_{coll} (3) components of a water-ethanol solution at a temperature 8 °C.

4. Research results and their discussion

It can be seen from Fig. 1 that, firstly, the total self-diffusion coefficient D remains smaller than the self-diffusion coefficient D_w of pure water in the entire range of studied concentrations. And only when $X \rightarrow 0$ it goes to D_w . Secondly, the main contribution (~ 75 %) to the total self-diffusion coefficient D of the solution of the water-ethanol belongs to its single-particle component D_{sp} . And, thirdly, the features inherent in the $D_{sp}(X)$ coefficient are also observed in the $D(X)$ coefficient. These are two minima in the concentration range $X = 0.04$ mol. particl. often and $X = 0.2$ mol. particl. At the same time, the time of the settled life of the molecule in the vibrational state τ_0 (Fig. 2) increases significantly, which is manifested in the form of two maxima. That is, at these concentrations, there is a significant decrease in the intensity of diffusion by a jump. The first minimum in $D(X)$ and $D_{sp}(X)$ has a smaller width and a larger amplitude compared to the second, which is quite possibly due to the different nature of the processes that determine them.

in detail in [14]. The quasielastic spectra obtained with regard to 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 ΔE of all the QENS spectra were determined, and the functional dependence $\Delta E(Q^2)$ which contains information about the diffusion processes in a liquid, is obtained. To analyze the $\Delta E(Q^2)$ dependences obtained based on 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 lifetime of a molecule is shown in Fig. 2.

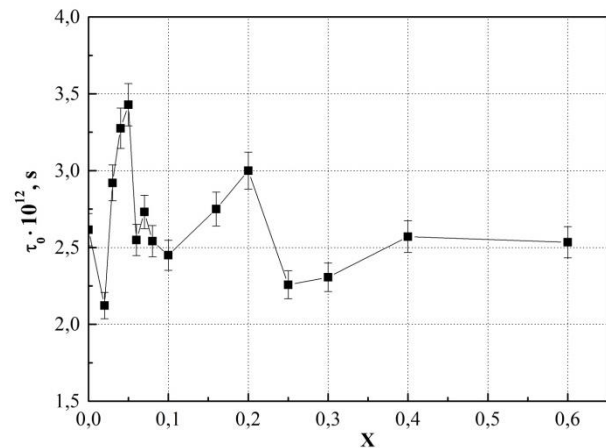


Fig. 2. Concentration dependence of the settled lifetime of the molecule in the vibrational state of the solution water-ethanol at a temperature 8 °C.

Fig. 1 also shows the collective component $D_{coll}(X)$ of the general self-diffusion coefficient, in which, as we can see, two minima are also observed, but of much smaller amplitude. In addition, they are shifted towards higher concentrations. The first minimum is at 0.06 mol. particl., and the second at ~ 0.25 mol. particl. Moreover, it is much wider than the first minimum.

The revealed features of the diffusion parameters, to a certain extent, can be explained based on the results of [5]. In it, considering aqueous solutions of glycerol, it is assumed that the anomalous properties of dilute aqueous solutions of alcohols are caused by the appearance of strong hydrogen bonds between water and alcohol molecules, which is accompanied by the intensive formation of clusters. The elementary cluster consists of two to three alcohol molecules and ten water molecules and has a size of ~ 6 Å. It is stable and it is suggested to consider it as a pseudo particle [5]. The appearance of clusters on the one hand causes an increase in the number of water molecules with increased binding energy (in the cluster). On the other hand, the process of solu-

tion clustering leads to a decrease in the number of molecules in the free volume of the solution. Both factors lead to a decrease in the intensity of the activation mechanism of the diffusion of water molecules and thus to a decrease in the single-particle component D_{s-p} of the total self-diffusion coefficient D and, accordingly, to an increase in the time of the settled life of the molecule at a concentration of 0.04 mol. part. (see Figs. 1 and 2).

Since the anomalous behavior of the diffusion characteristics depends not only on the concentration but also on the temperature of the solution, in this regard, the dynamics of the molecules of the water-

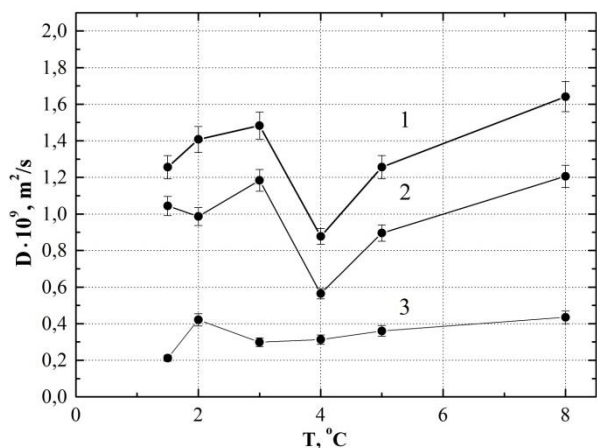


Fig. 3. Temperature dependence of the total self-diffusion coefficient D (1) and its single-particle D_{s-p} (2) and collective D_{coll} (3) components of a water-ethanol solution with a concentration of 0.04 mol. part.

In the vicinity of a temperature of 4 °C, a deep minimum is observed in the coefficients D and D_{s-p} . Time t at this temperature increases significantly. This indicates a significant decrease at a given concentration and temperature in the intensity of the activation mechanism of diffusion of solution molecules, which may be due to the binding of water and ethanol molecules into complexes (clusters). That is, in the vicinity of a temperature of 4 °C and a concentration of 0.04 mol. part. there is a singular point where the intensive formation of clusters consisting of 1 or 2 ethanol molecules and 6 ÷ 10 water molecules occurs.

The configuration of hydrogen bonds in the middle of an elementary cluster differs from those in the volume of water. The lifetime of such clusters is significantly longer than the time of molecular colli-

ethanol system were studied by the method of quasielastic scattering of neutrons as a function of temperature at a constant concentration of 0.04 mol. part. in the range of 1.5 °C - 8 °C. It is at this concentration that the diffusion movements of molecules in this solution are maximally slowed down (see Figs. 1 and 2). As in previous experiments, the total self-diffusion coefficient of molecules D , its single-particle D_{s-p} and collective D_{coll} components, and the time of the settled life of a molecule in the vibrational state τ were determined. Their temperature dependence is presented, respectively, in Figs. 3 and 4.

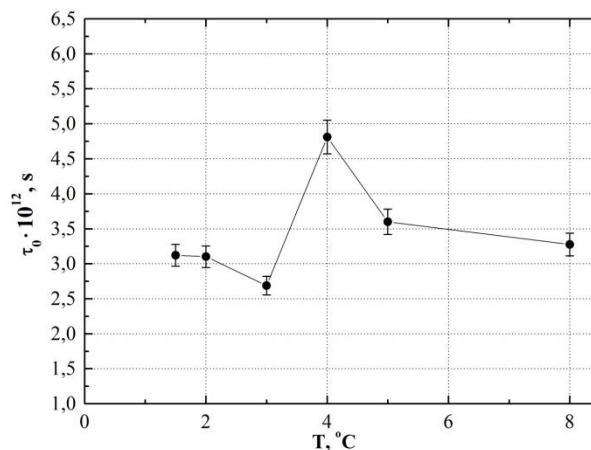


Fig. 4. Temperature dependence of the time of the settled life of a molecule in the equilibrium position of a solution of water-ethanol with a concentration of 0.04 mol. part.

sions and the lifetime of water clusters. Thus, this elementary cluster, as noted above, can be considered as a pseudo particle. The temperature deviation from 0.04 mol. part. sharply lowers the intensity of cluster formation and accelerates the destruction of existing complexes of water and ethanol molecules.

Therefore, using QENS in a dilute ethanol solution, a number of features were revealed in the concentration and temperature dependence of the total self-diffusion coefficient D and its single-particle component at a concentration of 0.04 mol. part. and a temperature of 4 °C, indicating the existence of a singular point here. However, its position does not coincide with light scattering data, according to which the singular point is located near 0.09 mol. part. often [7].

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НЕЙТРОННІ ДОСЛІДЖЕННЯ ДИФУЗІЙНИХ ПРОЦЕСІВ В ОКОЛІ ОСОБЛИВОЇ ТОЧКИ У РОЗБАВЛЕНОМУ ВОДНОМУ РОЗЧИНІ ЕТАНОЛУ

Проблема, що розглядається у даній роботі, стосується фізики рідин. Точніше фізики динамічних процесів у рідинах. Методом квазіпружного розсіяння повільних нейтронів досліджено динаміку молекул системи вода - етанол залежно від концентрації за температури 8 °С і залежно від температури при концентрації $X = 0,04$ мольних часток (мольн. част.). Визначено загальний коефіцієнт самодифузії молекул D , його одночастинкова D_{s-p} і колективна D_{coll} складові та час осілого життя молекули у коливному стані τ . Детально вивчено область малих концентрацій, де в околі концентрацій $X = 0,04$ мольн. част. і $X = 0,2$ мольн. част. у коефіцієнтах D та D_{s-p} виявлено два мінімуми. Час τ 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 у комплекси (кластери). Аналогічно в околі температури 4 °С у коефіцієнтах D та D_{s-p} виявлено глибокий мінімум. Час τ за цієї температури теж збільшується. Тобто, за температури 4 °С відбувається зниження інтенсивності активаційного механізму дифузії молекул розчину. Отже, при концентрації $X = 0,04$ мольн. част. і температурі 4 °С у системі вода - етанол існує особлива точка. Проте, її положення не збігається з даними з розсіяння світла.

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

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