LIQUIDS AND LIQUID CRYSTALS

SELF-DIFFUSION PROCESSES IN DILUTED WATER-ALCOHOL SOLUTIONS

N.P. MALOMUZH, K.N. PANKRATOV, E.L. SLINCHAK

I.I. Mechnikov Odesa National University, Faculty of Physics
(2, Dvoryans'ka Str., Odesa 65026, Ukraine; e-mail: selers@list.ru)

The concentration and temperature dependences of both the self-diffusion coefficient of water molecules in diluted water-ethanol solutions and its collective part have been discussed. The cluster model of the solution structure is used to explain nontrivial features in the behavior of the self-diffusion coefficient which is considered as a sum of contributions given by water molecules located inside and outside the clusters. The law describing the dependence of the total self-diffusion coefficient on the ethanol concentration has been found. The collective part of the self-diffusion coefficient and the residence time of water molecules are demonstrated to increase with the ethanol concentration. A model of elementary water-ethanol cluster has been proposed and physically substantiated. A careful comparison of theoretical results with experimental ones on the molecular light scattering (MLS) and the incoherent scattering of thermal neutrons has been carried out.

1. Introduction

Numerous experimental researches of diluted water-alcohol solutions reveal a number of anomalies in their properties similar to those observed near the critical
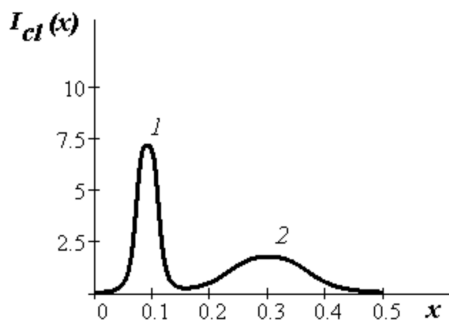

Fig. 1. Concentration dependence of the integral MLS intensity in a water-ethanol solution at a temperature of 20 °C: *1* – anomal peak, *2* – normal peak

point of lamination [1]. In particular, MLS in dissolved water-alcohol solutions with concentrations $0 < x < 0.1$ demonstrates an expressive additional maximum. At the same time, in a water-ethanol solution, two maxima are observed in the concentration dependence $I(x)$ of the integral intensity of scattered light [2, 3]: (i) an ordinary one (*2* in Fig. 1) located at the concentration $x \approx 0.3$ and caused by concentration fluctuations, and (ii) an anomal one (*1* in Fig. 1) at the concentration $x \approx 0.09$, the appearance of which is associated with the clusterization of the solution. The parameters of those two peaks are substantially different. The halfwidth of the anomal peak, if considered as a function of the concentration, is about an order of magnitude narrower, while the maximum of its intensity is, on the contrary, about an order of magnitude larger. A characteristic feature of the anomal peak in the water solution of ethanol is the growth of the light scattering intensity and a reduction of the concentration halfwidth with decrease in the temperature.

Since the solution is close to an ideal one in the specified concentration range [4], the appearance of the anomal peak cannot be explained without going beyond the limits of the simplest molecular concepts on the solution structure and properties. In work [5], arguments were put forward that the additional maximum in the low-concentration range is a consequence of the clusterization of a solution. The latter is initiated by the formation of strong hydrogen bonds between alcohol and water molecules. In the water-ethanol solution, the energies of hydrogen bonds between water molecules (≈ 0.19 eV [6]) and between alcohol molecules (≈ 0.21 eV [6]) are lower than the binding energy between water and ethanol molecules (≈ 0.25 eV [6]).

In work [5], such a behavior of the integral intensity was naturally explained by the presence of the processes of clusterization in the system. In particular, in water-alcohol solutions, hydrogen bonds make a few water molecules and a solute molecule to join. Clusters that are formed in such a way can be considered as impurity particles. If the solution concentration approaches a certain value, elementary clusters form a percolation cluster. The formation of the latter is accompanied by a destruction of the former. The interaction between elementary clusters creates conditions for the lamination of a solution. If the left-hand branch of the spinodal is located to the left from the percolation threshold, cluster concentration fluctuations start to grow substantially while approaching it (for more details, see work [7]). Therefore, the maximum of the MLS intensity is observed just when approaching the pseudospinodal of the system, the concentration range of which is confined from above by the percolation threshold. This circumstance manifests itself in MLS, nuclear magnetic resonance, and – as was shown in work [8] – thermal neutron scattering experiments.

In work [9], the results on quasielastic light scattering by slow neutrons in the water-ethanol solution were reported. Such an experiment allowed the total self-diffusion coefficient of water molecules to be determined and its collective part to be evaluated. According to the results of work [9], in the ethanol concentration range from 0.02 to 0.08, the total self-diffusion coefficient of water molecules has a minimum in the interval $0.05 < x < 0.06$ ($D_s \approx 1.65 \times 10^{-5}$ cm^2/s at $T = 281$ K). A similar minimum was also observed for the collective part of the self-diffusion coefficient at the concentration $x \approx 0.06$ ($D_0 \approx 0.2 \times 10^{-5}$ cm^2/s at $T = 281$ K). It was shown that the one-particle part of the self-diffusion coefficient monotonously grows as the concentration increases. A conclusion was drawn that it is the variation of the collective part only that is responsible for the concentration dependence of the total self-diffusion coefficient of water molecules.

We note that the authors of work [9] calculated the total self-diffusion coefficient of water molecules D_s and its collective part D_0 making use of experimental data for the halfwidth of quasielastic neutron scattering peak as a function of the squared wave-vector in the interval $0 \leq \mathbf{k}^2 \leq 10$ Å^{-2}, which goes substantially beyond the applicability region of the diffusion approximation [8,10].

This work aimed at (i) describing the structure of elementary water-ethanol clusters and estimating their dimensions, (ii) analyzing the features of MLS in water-ethanol solutions, (iii) determining the pseudospinodal and finding the cluster percolation threshold, and (iv) describing the concentration dependence to the self-diffusion coefficient and comparing the latter with the results of neutron scattering experiments.

2. Structure and Dimension of Elementary Cluster

Let us consider the structure of an elementary cluster formed by water and ethanol molecules and estimate its dimension. Since the ethanol molecule contains a hydroxyl group (– OH), it is the protons of atoms the hydroxyl is composed of that are the most capable to form hydrogen bonds with water molecules. Owing to the presence of water molecules, the alcohol ones join one another to form clusters.

We simulated a cluster making use of the HyperChem_7.0 computer code. One to ten ethanol molecules were considered to be distributed in a definite volume. If the number of alcohol molecules exceeded one, the geometrical optimization of the relative arrangement of molecules was carried out. Then a certain number of water molecules were added to this volume. The molecules that did not form hydrogen bonds were not included into the cluster. The most adequate turned out the model, in which the cluster contained two ethanol and about six water molecules. The criterion for the selection of a cluster type was the minimal number of hydrogen bonds that provided the stability of a cluster. The further increase of the number of alcohol and water molecules did not influence the formation and the number of hydrogen bonds essentially.

Such a consideration brought us to the conclusion that an elementary cluster contains two molecules of alcohol and approximately six water molecules. The dimension r_0 of such a cluster is approximately 5 to 6 Å. One of the possible versions of an elementary cluster is shown in Fig. 2.

The formation of clusters depends on the temperature of a solution and its concentration, because clusters are formed until their number exceeds the percolation threshold value for spherical particles. After that, clusters start to interact with one another, and the clusterization process in the solution essentially changes.

According to the results of work [7], at concentrations below the percolation threshold ($x < x_p$), the cluster-induced osmotic pressure can be approximated by the
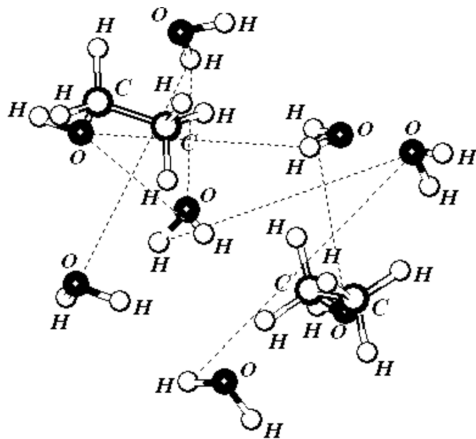
Fig. 2. Plane projection of an elementary cluster in the water-ethanol solution (dotted lines denote hydrogen bonds inside the cluster)

van der Waals equation

$$p_{\text{osm}}(v) = \frac{k_{\text{B}}T}{v - v_0} - \frac{a}{v^2}, \tag{1}$$

where v is the volume per cluster, $v_0 = 4v_{\text{cl}} = b$, and v_{cl} is the own volume of the elementary cluster [11].

The integral MLS intensity is connected with the osmotic pressure by the relation

$$I_a \approx \frac{T}{A}, \tag{2}$$

where

$$A = \frac{\partial p_{\text{osm}}(v)}{\partial v}. \tag{3}$$

Since $v = n_{\text{cl}}^{-1}$, where n_{cl} is the cluster concentration (it is determined by the relation $n_{\text{cl}} \approx x n_{\text{w}}/z_{\text{et}}$, where z_{et} and n_{w} are the number of ethanol molecules in the elementary cluster and the concentration of water molecules, respectively), formula (3) can be rewritten as follows:

$$p_{\text{osm}}(x) = \frac{k_{\text{B}}T n_{\text{w}} x}{z_{\text{et}} - 4v_{\text{cl}} n_{\text{w}} x} - a \left(\frac{x n_{\text{w}}}{z_{\text{et}}} \right)^2. \tag{4}$$

The scope of validity for this expression is determined by the inequality

$$x < \frac{z_{\text{et}}}{4v_{\text{cl}} n_{\text{w}}}.$$

Since the maximum of the MLS intensity is observed at the concentration $x \approx 0.09$, we adopt that this value corresponds to the maximal concentration, at which

elementary clusters still remain stable. The increase of the concentration gives rise to a destruction of elementary clusters. That is why the value of the parameter z_{et} is confined from below:

$$0.36 n_{\text{w}} v_{\text{cl}} < z_{\text{et}}. \tag{5}$$

In particular, if the dimension (radius) of the cluster $r_0 \approx 3 \div 5$ Å, formula (5) gives

$$z_{\text{et}} > 1.4 \div 3.2.$$

Hence, the optimization of the relative arrangement of water and alcohol molecules in the cluster and the analysis of the equation of state give rise to the conclusion that an elementary cluster in an water solution of ethanol should contain at least two alcohol molecules. Such an estimate completely agrees with the cluster model presented in Fig. 2.

Now, let us formulate additional arguments that put our assumptions on the structure of a clustered solution and its behavior into agreement. We note that the dimension of a cluster in a water-ethanol solution can be calculated similarly to what was made in work [7].

It is expedient to change over to the dimensionless variables

$$\widetilde{T} = \frac{T}{T_m}, \quad \widetilde{p}_{\text{osm}}(x) = \frac{p_{\text{osm}}(x) z_{\text{et}}}{n_{\text{w}} k_{\text{B}} T_m}, \quad \widetilde{a} = \frac{a}{a_0},$$

$$\widetilde{b} = \frac{16\pi r_0 n_{\text{w}}}{3 z_{\text{et}}}, \quad a_0 = \frac{k_{\text{B}} T_m z_{\text{et}}}{n_{\text{w}}},$$

where T_m is the water crystallization temperature, and $\tilde{a}$ and $\tilde{b}$ are the parameters that characterize the cluster-to-cluster interaction and the dimensions of clusters, respectively. Now, the van der Waals equation (4) takes the form

$$\widetilde{p}_{\text{osm}}(x) = \frac{x\widetilde{T}}{1 - \widetilde{b}x} - \widetilde{a}x^2. \tag{6}$$

In order to evaluate the constants $\tilde{a}$ and $\tilde{b}$, we used the experimental data on MLS in the water-ethanol solution reported in works [2, 3]. The least-squares method was used to approximate the integral-intensity function and to calculate the parameters $\tilde{a}$ and $\tilde{b}$. The obtained values for those parameters and for the size of the elementary cluster in the water-ethanol solution, $r_0 = 3\tilde{b}z_{\text{et}}/(16\pi n_{\text{w}})$, are resulted in Table 1.

T a b l e 1

$\tilde{a}$	$\tilde{b}$	$r_0 \times 10^8$, cm
0.28	31.02	4.81

Comparing the cluster dimensions calculated in such a way with those given by the geometrical model, we come to the conclusion that the radius of an elementary cluster in the aqueous solution of ethanol is about 5 Å.

3. Pseudospinodal and Percolation Threshold

Let us evaluate the concentration at the percolation threshold. When coming closer to it, the interaction between elementary clusters gets stronger, which is accompanied by the cluster destruction.

According to the results of work [7], we calculate the position of the percolation-threshold concentration x_p by the formula

$$x_p = \frac{\varphi_p}{v_{\mathrm{cl}} n_{\mathrm{w}}}. \tag{7}$$

For the water-ethanol solution, the limiting value of concentration, at which stable clusters still exist, is $x_p \approx 0.097$.

Fluctuations grow anomalously, if the state of the system approaches the left-hand branch of its pseudospinodal, corresponding to the lamination in the solution of elementary clusters; the latter is described by either the equations $x_s = x_s(T)$ or $T_s = T_s(x)$, depending on which parameter—temperature or concentration—is maintained constant. Note that the water solution of ethanol is associated with an "unattainable" upper critical point (see Fig. 3), which is in agreement with the behavior of the temperature dependence of the MLS intensity. If the temperature of the solution increases, the MLS intensity diminishes. This fact can be connected with the destruction of elementary clusters, the fluctuation concentrations of which are the origin of MLS.

The range of application of the developed approach – in (T, x)-coordinates – is confined by the ordinate axis $(x = 0)$ from the left-hand side, by the straight line $x = x_p$ from the right-hand side, by the crystallization curve $T_{\mathrm{cr}} = T_{\mathrm{cr}}(x)$ from below, and by the straight line $T = T_p$ from above, where T_p is the root of the equation

$$x_s(T_p) = x_p. \tag{8}$$

Beyond this region, elementary clusters become unstable, so that the proposed theory cannot explain the phenomena observed here.
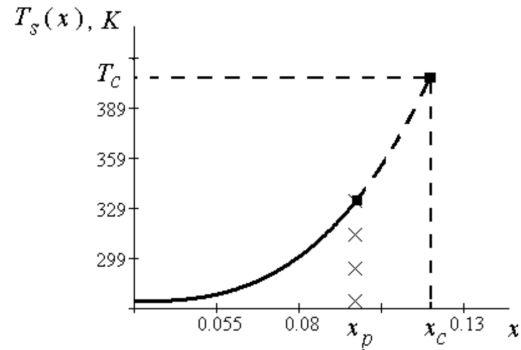

Fig. 3. Concentration dependence of the pseudospinodal position for a water-ethanol solution

4. Self-Diffusion of Water Molecules in the water-ethanol Solution in the Intensive clusterization Range

The formation of clusters should be accompanied by a reduction of the translational mobility of water molecules and the molecules of dissolved alcohol. According to the assumptions formulated above, some part of water molecules in a clustered solution enters into the cluster structure, while the other one forms mutual hydrogen bonds. Taking into account that the mole concentration of water molecules in clusters is equal to $xz_{\mathrm{w}}/z_{\mathrm{et}}$ (here, z_{w} is the number of water molecules), the self-diffusion coefficient of water molecules in the solution, $D_s^{(\mathrm{w})}$, looks like

$$D_s^{(\mathrm{w})} = D_s^{(0)}\left(1 - \frac{z_{\mathrm{w}}}{z_{\mathrm{et}}}x\right) + D_s^{(\mathrm{cl})}\frac{z_{\mathrm{w}}}{z_{\mathrm{et}}}x. \tag{9}$$

Here, $D_s^{(0)}$ is the self-diffusion coefficient of water molecules in pure water, and $D_s^{(\mathrm{cl})}$ is the self-diffusion coefficient of water molecules in the cluster. These two coefficients, by their order of magnitude, are related to each other by the relation

$$D_s^{(\mathrm{cl})} \approx D_s^{(0)}\frac{r_{\mathrm{w}}}{r_0}, \tag{10}$$

where r_{w} and r_0 are the radii of a water molecule and a cluster, respectively. It should be noted that formula (9) for $D_s^{(\mathrm{w})}$ describes experimental values quite satisfactorily at concentrations $x \ll x_s$.

In the case where the system approaches the pseudospinodal ($x \approx x_s$), formula (10) is to be corrected. This circumstance is explained by the fact that, while coming closer to the pseudospinodal, the positions and the motions of elementary clusters begin to correlate strongly (the correlation length r_c becomes substantially larger). For this reason, the self-diffusion coefficient of
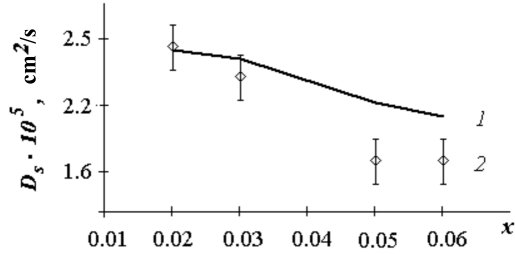
Fig. 4. Concentration dependence of the total self-diffusion coefficient of water molecules in the water-ethanol solution: *1* – values calculated by formulas (9) and (12), *2* – the experimental data taken from work [7]

water molecules in elementary clusters will be defined by the relation

$$D_s^{(cl)} \approx D_s^{(0)} \frac{r_0}{r_c}. \qquad (11)$$

The ratio r_0/r_c substantially decreases near the pseudospinodal owing to the correlation length growth [12]; therefore, the other contribution to the self-diffusion coefficient $D_s^{(w)}$ (formula (9)) can be neglected.

In work [9], the experiment was carried on at the temperature $T = 281$ K. At this temperature, the concentration x at the pseudospinodal is approximately equal to 0.06 (see Fig. 3). At this value, the self-diffusion coefficient is also expected to be minimal. The experimental minimum is observed at the concentration $x \approx 0.05 \div 0.06$. This means that the self-diffusion coefficient of water molecules $D_s^{(w)}$ in the water-ethanol solution can be determined making use of the relation

$$D_s^{(w)} \approx D_s^{(0)} \left(1 - \frac{z_w}{z_{et}} x\right). \qquad (12)$$

A comparison of the results calculated by formula (12) is presented in Fig. 4. Some discrepancy between the theoretical and experimental values of the self-diffusion coefficient of water molecules $D_s^{(w)}$ in the water-ethanol solution can be naturally explained by the fact that the hydration spheres emerge around water-ethanol clusters. For the calculation results and the experimental data to be in agreement, we must put $z_w \approx 8 \div 10$, i.e. the number of hydrated molecules should be 2 to 4. Below, we intend to give more sound arguments to prove this conclusion.

5. Improved Values for the Characteristic Parameters of Thermal Motion of Water Molecules in water-alcohol Solutions

As was indicated in Introduction, the authors of work [9] used experimental data from the interval of squared wave-vector values $0 \leq \mathbf{k}^2 \leq 10$ Å^{-2} for the determination of the collective part of the self-diffusion coefficient D_0 and the residence time τ_0. This interval goes far beyond the diffusion approximation and, hence, beyond the applicability region of the Singvi–Sjolander–Oskotskii theory [13,14].

To determine the parameters concerned, we used experimental values for the halfwidth γ_D of the peak of incoherent scattering of thermal neutrons from the interval $0 \leq \mathbf{k}^2 \leq 1$ Å^{-2}, as well as the expansion of this quantity in a power series in $\mathbf{k}^2$ which was obtained in work [15]:

$$\gamma_D \approx D_s^{(w)} \mathbf{k}^2 - \tau_0 D_1^2 \mathbf{k}^4 + \tau_0^2 D_1^3 \mathbf{k}^6 + \ldots \qquad (13)$$

Here, $D_s^{(w)}$ is the total self-diffusion coefficient of water molecules, and D_1 is its one-particle part [10, 15]. The values of the collective part of the self-diffusion coefficient, $D_0 = D_s^{(w)} - D_1$, and the residence time were obtained by fitting dependence (13) to experimental data; the corresponding results are listed in Table 2. Here, for the sake of comparison, we also present values for the collective part $D_0^{(B)}$ of the self-diffusion coefficient which were determined in work [8].

One can see that, in the case of the water solution of ethanol, the D_0-values slowly grow with the alcohol concentration. From the viewpoint of our concept of the mechanism that underlies the dependence of the density of elementary clusters on their concentration in the solution, such a growth of D_0 seems quite natural. On the contrary, a reduction of D_0 with increase in the concentration – as was discussed in work [9] – is problematic to explain.

The increase of the residence time by about 70% with increase in the ethyl alcohol concentration also agrees well with the cluster model of the solution structure.

T a b l e 2. **Total self-diffusion coefficient, its collective part, and the residence time for a water-ethanol solution**

	Mole concentration		
	0.02	0.03	0.05
$D_s^{(w)} \times 10^5$, cm^2/s	2.17	2.03	1.65
$D_0 \times 10^5$, cm^2/s	0.42	0.48	0.52
$\tau_0 \times 10^{13}$, s (by Eq. (12))	5.00	6.50	8.50
$D_0^{(B)} \times 10^5$, cm^2/s [9]	0.75	0.70	0.25

6. Conclusions

The consideration of the formation of clusters in diluted aqueous solutions of ethyl alcohol is the main topic of this work. We explain the anomal growth of concentration fluctuations in a diluted solution as a manifestation of the approach of the system to the left-hand branch of its pseudospinodal. The behavior of the system depends on the relative position of its pseudospinodal with respect to the percolation threshold. If the concentration in the system comes closer to its percolation threshold x_p, elementary clusters are destroyed. Therefore, the behavior of the solution essentially changes beyond this range (i.e. at $x > x_p$).

Experimental studies in work [9] were carried out at the temperature $T = 281$ K; the latter corresponds to a pseudospinodal with $x_s \approx 0.062$. The percolation threshold is expected to be located at the higher concentration $x_p \approx 0.097$, and this circumstance justifies the eligibility of our approach.

We demonstrated that an elementary cluster contains about six water and two alcohol molecules. The radius of such a cluster is approximately equal to 5 Å, which is in agreement with the proposed computer model. At the same time, for a better agreement between the experimental and calculated data, we put forward a supposition that an elementary cluster is surrounded by a hydration sphere that contains 2 to 4 water molecules.

The cluster model makes it possible to explain the concentration dependence of the total self-diffusion coefficient $D_s^{(w)}$ of water molecules and its collective part D_0. The appearance of $D_s^{(w)}$-minimum near the pseudospinodal is explained by a substantial reduction of the translational mobility of clusters due to the fast growth of the correlation length. The self-consistent growth of D_0 and τ_0 also testifies in favor of our concept of the structure of the solution.

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ПРОЦЕСИ САМОДИФУЗІЇ В РОЗБАВЛЕНИХ ВОДНО-СПИРТОВИХ РОЗЧИНАХ

М.П. Маломуж, К.М. Панкратов, О.Л. Слинчак

Р е з ю м е

Обговорюються концентраційна і температурна залежності коефіцієнта самодифузії молекул води та його колективної складової в розбавлених розчинах вода–етанол. Для пояснення нетривіальних особливостей поведінки коефіцієнта самодифузії використовуються кластерні уявлення про структуру розчину. Згідно з цим коефіцієнт самодифузії молекул води представлено у вигляді суми внесків, зумовлених молекулами води, розміщеними всередині та ззовні кластерів. Встановлено закон залежності повного коефіцієнта самодифузії від концентрації етанолу. Показано, що колективна складова коефіцієнта самодифузії та час осілого життя молекул води зростають зі збільшенням концентрації етанолу. Запропоновано і фізично обґрунтовано модель елементарного водно–етанолового кластера. Виконано ретельне порівняння теоретичних результатів з результатами експериментів з молекулярного розсіяння світла та некогерентного розсіяння теплових нейтронів.