

PECULIARITIES OF THE DIFFUSION PROCESS IN DILUTE WATER-TREHALOSE SOLUTIONS

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In the present work, the main attention is focused on the temperature dependence of the diffusion coefficient D in dilute water-trehalose solutions. It is shown that the peculiarities of this phenomenon are mainly connected with the destruction of the water H-bond network in the thin layer around admixture particles and the appearance of a new contribution to the potential of their interactions. As a result, the last changes its sign, transforming from the attractive to repulsive potentials when temperature increases. The consecutive description of all factors, influencing the temperature dependence of D , is given.

Introduction

Water-trehalose solutions were the object of numerous investigations (see [1–3]). Many nontrivial thermodynamic and kinetic properties were observed. So the diffusion coefficient $D(\varphi)$, measured in the PCS-experiments, shows a surprising behavior. At small φ , the diffusion coefficient increases and reaches a maximum value at some $\varphi_m(T)$. Then it begins to quickly decrease. It is clear that a similar behavior has no explanation within the simplest representations of the diffusion process.

In addition, it was shown in [4] that, for small φ , $\varphi < 0.1$, the coefficient k_D in the equation

$$D(\varphi) = D(0)(1 + k_D\varphi + \dots) \quad (1)$$

changes its sign at some temperature $T_D = 308$ K (see Fig.1). The last is negative at $T \leq T_D$ and positive at $T \geq T_D$. Unfortunately, even this effect has no simple explanation. Indeed, in general case, the diffusion coefficient takes the structure:

$$D(\varphi) = D(0) \frac{g(\varphi)}{g(0)} \frac{1}{k_B T} \frac{\partial P(n)}{\partial n}, \quad (2)$$

where $P(n)$ is the osmotic pressure as a function of the density n of admixture molecules and $g(\varphi)$ is their mobility. The mobility of particles diminishes when the volume fraction φ increases. This effect is often described by the relation

$$g \sim \frac{1}{\bar{\eta}(\varphi)r_0}, \quad (3)$$

where $\bar{\eta}(\varphi)$ is the average shear viscosity and r_0 is the radius of a particle. To estimate $P(n)$ and its density derivatives, one can use the van der Waals equation

$$P = \frac{nk_B T}{1 - nv_0} - an^2,$$

in which $v_0 = 4v_m$, where v_m is the volume of an admixture particle. Within these assumptions, the coefficient k_D is

$$k_D = 2 \left(\frac{v_a}{v_m} - \frac{5}{4} \right)$$

where

$$v_a = v_0 - \frac{a}{k_B T}.$$

In principle at $T = T_0$, where

$$T_0 = \frac{4a}{11k_B v_m},$$

the coefficient k_D , taking the representation

$$k_D = \frac{11}{4} \left(1 - \frac{T_0}{T} \right),$$

can change its sign, becoming positive at $T > T_0$. However its temperature dependence is too weak in comparison with that observed in [4].

From physical point of view, it is explained by several causes. First, the coefficient k_D is connected with the interparticle potential which includes both the van der Waals and dipole-dipole interactions. The spontaneous dipole moment of the “trehalose molecule + surrounding water” complex arises due to specific fluctuations of the H-bond network near a trehalose molecule and to the hydration effects. To estimate their role, we assume that a trehalose molecule changes the orientations of water molecules only in the monomolecular surface layer. The number ζ_H of water molecules falling in the last is about

$$\zeta_H \sim \left(\frac{r_0}{r_w} \right)^2 \sim (20 \div 30), \quad (4)$$

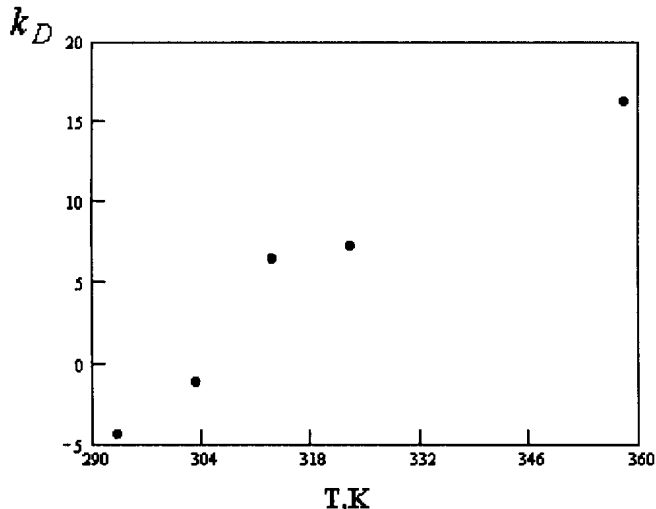


Fig. 1. Temperature dependence of the coefficient k_D , according to experimental data [4]

where r_w is the intermolecular spacing in water. Since $\zeta_H \gg 1$, we expect that the dipole-dipole contribution to the interparticle potential will be considerable. This contribution together with that of the H-bond network should be sensible to the variations of temperature. This effect will be discussed in detail below.

Note that the usage of the average shear viscosity in (2) is not justified, since the last is correctly defined only on scales essentially more than the interparticle spacing. On the other hand, the approximation $g(\varphi) \sim \frac{1}{\eta_0 r_0}$, where η_0 is the shear viscosity of a solvent, does not take into account the effects of reciprocal hydrodynamic influence of particles.

In [5], the nontrivial volume fraction dependence of the diffusion coefficient in PCS-experiments is qualitatively explained within the hydrodynamic approach, in which the mobility of a molecule depends on the effective shear viscosity. The last is defined as the proportionality coefficient between the moment of forces applied to a particle and its angular velocity. The viscosity defined in such a way differs from the shear viscosity of a solvent and the average shear viscosity of a solution. We want to emphasize here that the effective shear viscosity determines the behavior of both the mobility and the self-diffusion coefficient of admixture particles.

The present paper is devoted to the detailed investigation of the temperature dependence of k_D .

1. Effective and Average Shear Viscosities

Our discussion of the experimental data obtained in [4] is based on the results of [5, 6]. There, a new version of the cell approach to the shear viscosity of suspensions was developed. The most characteristic differences of it from the cell approaches proposed in [5, 6] are the following: a) instead of the translational motion of a particle in the spherical cell [7] its rotational motion is considered; b) the volume fraction dependence of the cell size is introduced. Due to the first circumstance, the symmetries of the spherical cell and corresponding hydrodynamic flows are coordinated better in comparison with [7]. The second assumption allows us to agree the results of the cell approach and those obtained with the help of hydrodynamic perturbation theory [8]. As a result, the applicability region of our approach becomes wider in comparison with [7, 8]. In [6], it was shown that the behavior of the average shear viscosity of suspensions can be successfully described up to $\Phi \simeq 0.45$, where Φ is the volume fraction of admixture particles proportional to φ (see below). The last value of Φ is close to $\Phi_* \simeq 0.49$ corresponding to the occasional packing of hard spheres.

In [9], an interpolation formula for the average shear viscosity of suspensions for $0 \leq \Phi \leq 0.5$ is proposed. However, its applicability in the hydrodynamic region is grounded only for $0 \leq \Phi \leq 0.25$.

One of the main results of [6] is the definition and detailed description of the so-called effective shear viscosity. The last is defined as the proportionality coefficient between the angular velocity $\vec{\Omega}$ of a particle and the moment of forces \vec{M} applied to the same particle to support the fixed value of $\vec{\Omega}$:

$$\vec{M} = 8\pi\eta_{\text{eff}} r_0^3 \vec{\Omega}.$$

The average shear viscosity $\bar{\eta}$ is determined from the balance equation

$$\frac{\eta_0}{2} \int_{V_{\text{cell}}} g_{ik}^2 dV = \frac{\bar{\eta}}{2} \int_{V_{\infty}} \bar{g}_{ik}^2 dV$$

for the dissipation energies. On the left side, η_0 is the shear viscosity of a solvent, $g_{ik} = \frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i}$ is the velocity gradient tensor for incompressible liquid, V_{cell} is the cell volume. On the right side, \bar{g}_{ik} is the velocity gradient tensor obtained by the averaging of g_{ik} over the volume $V \approx V_{\text{cell}}$, V_{∞} is the volume outside a particle.

In fact, V_∞ is the cell volume for the infinitely diluted liquid, whose shear viscosity equals $\bar{\eta}$.

Note that the shear viscosity measured in viscosimetric experiments, coincides with $\bar{\eta}$, since the characteristic scales of a viscosimeter are considerably more than the radius R of a cell. Unlike this, the behavior of the self-diffusion coefficient is determined by the effective shear viscosity that follows directly from the inequality $r_0 \leq R$ for the sizes of a particle and a cell. As follows from [6], the effective shear viscosity at small φ has the structure

$$\eta_{\text{eff}}(\Phi) = \eta_0(1 + 6.25\Phi^2 + \dots) \quad (5)$$

and thus does not include the term linear in Φ as $\Phi \rightarrow 0$, which is the most important feature of it.

Such a behavior of the effective shear viscosity is the necessary condition to explain the appearance of a maximum in the Φ -dependence of the diffusion coefficient [5].

The usage of hydrodynamic methods to describe the peculiarities of the shear viscosity and diffusion coefficient in water-trehalose solutions is possible because the size of an admixture molecule is essentially more in comparison with that for water. The shape of a trehalose molecule (see Fig. 2.) can be approximated by the spherical one with the initial radius $r_0 \approx 6 \text{ \AA}$. Here, it is appropriate to discuss this question in more detail.

It follows from the geometric structure of a trehalose molecule that r_0 is close to 6 \AA . A rather lesser value of r_0 is obtained from the mass estimate: $r_0 = \left(\frac{3}{4\pi} \frac{m_{\text{tr}}}{\rho_{\text{tr}}}\right)^{1/3}$, where m_{tr} and ρ_{tr} are the mass of a trehalose molecule and the density of the trehalose matter, respectively.

In such a way, we obtain $r_0 \approx 5.2 \text{ \AA}$. The value $r_0 \approx 6 \text{ \AA}$ is more preferable since the shape of a molecule is spherical only approximately. Due to the hydration effect, the effective radius of a trehalose molecule should grow.

2. Connection of the Volume Fraction with the Hydration Effect

In the previous section, we have noted that the behavior of the effective and average shear viscosities is determined by the volume fraction Φ of admixture particles. With satisfactory accuracy, the volume fraction Φ can be determined by the formula

$$\Phi = \frac{\left(\frac{M_t}{\rho_t} + \frac{M_w}{\rho_w} n_H\right) n_t}{\frac{M_t n_t}{\rho_t} + \frac{M_w n_w}{\rho_w}},$$

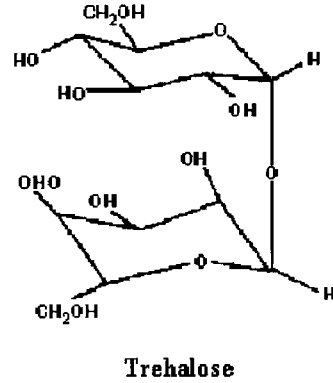


Fig. 2. Structure of a trehalose molecule $C_{12}H_{22}O_{11}$

where M_t and M_w are the molecular masses of trehalose and water, n_t and n_w are the number densities of trehalose and water molecules in water-trehalose solutions, n_H is the hydration number of water molecules (joined with a trehalose molecule). The variables ρ_t and ρ_w are the mass densities of a trehalose melt and pure water.

It is not difficult to see that

$$\Phi = \left(1 + \frac{M_w}{M_t} \frac{\rho_t}{\rho_w} n_H\right) \varphi, \quad (6)$$

where

$$\varphi = \frac{\frac{M_t}{\rho_t} n_t}{\frac{M_t n_t}{\rho_t} + \frac{M_w n_w}{\rho_w}} \quad (7)$$

is a volume fraction of the ideal solution. At $\rho_t \simeq \rho_w$, formulas (6) and (7) can be rewritten as

$$\Phi = \left(1 + \frac{M_w}{M_t} n_H\right) \varphi,$$

where

$$\varphi = \frac{M_t n_t}{M_t n_t + M_w n_w}.$$

Namely this parameter was used in [4] for the description of experimental data. The ratio

$$\frac{M_w}{M_t} = 0.05259.$$

The effective radius r_{eff} of the “trehalose molecule+hydrated water molecules” complex can be determined by the formula

$$r_{\text{eff}} = r_0 \left(\frac{\Phi}{\varphi}\right)^{1/3}. \quad (8)$$

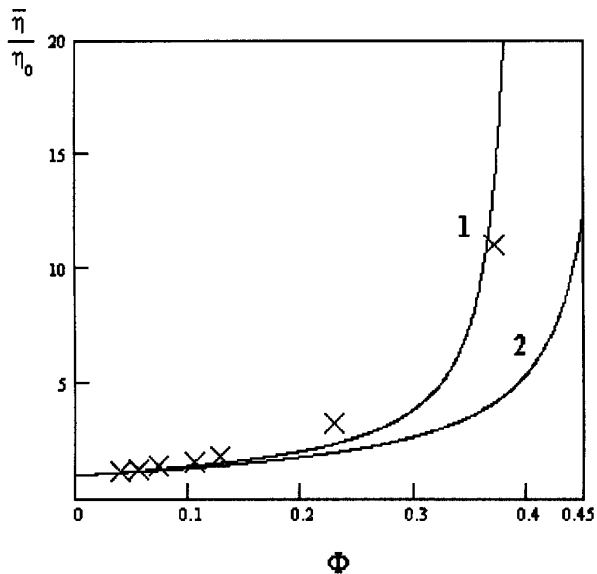


Fig. 3. Role of the hydration effects in the formation of the average shear viscosity: curve 1 corresponds to $n_\eta = 2.9$, curve 2 – $n_\eta = 0$. Both curves correspond to $T = 358$ K

Note that values of the hydration number n_H , manifested in the thermodynamic and kinetic processes should be rather different. In nonequilibrium phenomena n_H is identified with the number of water molecules involved by a trehalose molecule in its motion. This number n_H is expected to be less in comparison with that characteristic of quasistatic thermodynamic processes as well as ultrasonic experiments. Values of the hydration number n_η characteristic of the viscous processes, the effective radius of a trehalose molecule measured in viscosimetric experiments, and the limit values $\bar{\varphi}$ of the volume fraction for the applicability of the cell approach are presented in Table 1. The influence of the hydration effects is seen in Fig. 3.

3. Multipole-multipole Interaction between Trehalose Molecules

As noted above, the interaction between trehalose molecules in water is caused by the van der Waals forces and ones of the electric fluctuation nature. Indeed, due to the destruction of the H-bond network in water around a trehalose molecule, the last acquires a nonzero dipole moment and electric moments of higher orders. As a result, the additional fluctuation multipole-multipole mechanism (FMM) of intermolecular interaction arises. In general, it is necessary to take into account both spontaneous and induced multipole moments. They lead to the contributions to the intermolecular potential

which have different dependences on temperature and the molecular size and can even differ by their signs. The resulting intermolecular potential can have both the attractive and repulsive character. The role of the FMM-interaction in different systems (micellar, colloid, and emulsion solutions) was discussed in detail in [10,11].

To demonstrate the influence of main factors, let us consider the dipole-dipole interaction between two admixture molecules. In this approximation, the interaction energy

$$W(r|\vec{d}_1, \vec{d}_2) = \frac{1}{\varepsilon_1 r^3} \left[\vec{d}_1 \vec{d}_2 - 3 \frac{(\vec{d}_1 \vec{r})(\vec{d}_2 \vec{r})}{r^2} \right],$$

where \vec{d}_i is the dipole moment of the i th particle equal to the sum of spontaneous ($\vec{d}_i^{(s)}$) and induced ($\vec{d}_i^{(I)}$) dipole moments,

$$\vec{d}_i = \vec{d}_i^{(s)} + \vec{d}_i^{(I)}, \quad i = 1, 2,$$

and ε_1 is the dielectric permittivity of water. To calculate the average energy of intermolecular interaction, caused by spontaneous dipole moments, we can use the following approximation for the distribution function of dipole moments:

$$g(r|\vec{d}_1^{(s)}, \vec{d}_2^{(s)}) = (1 - W(r|\vec{d}_1^{(s)}, \vec{d}_2^{(s)})),$$

where $\beta = \frac{1}{k_B T}$. In such a way, we obtain

$$U^{(ss)}(r) = \langle W(r|\vec{d}_1^{(s)}, \vec{d}_2^{(s)}) \rangle = -\frac{2}{3} \frac{\langle (\vec{d}_i^{(s)})^2 \rangle^2}{\varepsilon_1^2 r^6}. \quad (9)$$

The contribution

$$U^{(sI)}(r) = \langle W(r|\vec{d}_1^{(s)}, \vec{d}_2^{(I)}) \rangle + \langle W(r|\vec{d}_1^{(I)}, \vec{d}_2^{(s)}) \rangle$$

caused by the spontaneous and induced dipole moments of two identical molecules is equal to

$$U^{(sI)}(r) = \frac{2}{\varepsilon_1 r^3} \left\langle \left[(\vec{d}_1^{(s)} \vec{d}_2^{(I)}) - 3 \frac{(\vec{d}_1^{(s)} \vec{r})(\vec{d}_2^{(I)} \vec{r})}{r^2} \right] \right\rangle. \quad (10)$$

One can show that the induced dipole moment of the second particle in the electric field of the first one is

Table 1. Values of the effective radius r_{eff} calculated according to (6) and (8) and the hydration number n_η as well as $\bar{\eta}$ for various temperatures

T, K	r_η	n_η	$\bar{\varphi}$
293	6.1	1.2	0.463
313	6.23	2.3	0.425
333	6.3	3	0.419

determined by the expression

$$\vec{d}_2^{(I)} = \frac{\varepsilon_1 - \varepsilon_2}{2\varepsilon_1 + \varepsilon_2} \left(\frac{r_0}{r}\right)^2 \left[\vec{d}_1^{(s)} - 3 \frac{(\vec{d}_1^{(s)} \vec{r}) \vec{r}}{r^2} \right], \quad (11)$$

where ε_2 the dielectric permittivity of the trehalose substance, $\varepsilon_2 < (\ll) \varepsilon_1$. Substituting (11) to (10) and averaging over possible orientations and values of $\vec{d}_1^{(s)}$, we get

$$U^{(sI)}(r) = \frac{4}{\varepsilon_1} \frac{1 - \tilde{\varepsilon}}{2 + \tilde{\varepsilon}} \frac{\langle (\vec{d}_1^{(s)})^2 \rangle}{r_0^3} \left(\frac{r_0}{r}\right)^6, \quad \tilde{\varepsilon} = \frac{\varepsilon_2}{\varepsilon_1}. \quad (12)$$

The contribution

$$U^{(II)}(r) = \langle W(r | \vec{d}_1^{(I)}, \vec{d}_2^{(I)}) \rangle$$

decays proportionally to $\left(\frac{r_0}{r}\right)^9$ and can be ignored.

From physical point of view, the contributions $U^{(ss)}(r)$ and $U^{(sI)}(r)$ to the interparticle potential have the same origin as the standard van der Waals potential [11]. The difference between them is only caused by different scales of electromagnetic fluctuations which are taken into account. In particular, their characteristic times increase from $(10^{-15} \div 10^{-14})$ s for the van der Waals interaction up to $(10^{-12} \div 10^{-11})$ s for one considered above.

It is necessary to note that $U^{(ss)}(r)$ and $U^{(sI)}(r)$ have different characters: $U^{(ss)}(r)$ is the attractive potential, $U^{(sI)}(r)$ — repulsive one. In addition, they have different dependences on ε_1 and r_0 . Considering $U^{(ss)}(r)$ and $U^{(sI)}(r)$ as functions of r_0 , we see from (9) and (12) that

$$|U^{(ss)}(r)| < U^{(sI)}(r)$$

at $r_0 > r_*$, where $r_* = \left(\frac{d_w^2}{6\varepsilon_1 k_B T}\right)^{1/3} \xi^{2/3}$, d_w is the dipole moment of a water molecule, and $\xi^2 = \frac{\langle (\vec{d}_1^{(s)})^2 \rangle}{d_w^2}$. At the temperature $T_m = 273$ K of the water crystallization,

$$r_* \simeq 0.6 \cdot 10^{-8} \xi^{2/3} \text{ cm.}$$

Putting $\xi \sim (10 \div 25)$, we get the estimate

$$r_* \sim (2 \div 4) \cdot 10^{-8} \text{ cm.}$$

Since the molecular radius of a trehalose molecule ($r_0 \sim 6$) Å is noticeably more, we conclude that the interaction between two trehalose molecules has the repulsive character.

Let us consider the following terms of the asymptotic expansion for the fluctuation multipole-multipole interaction between two particles. For this purpose, it is expedient to use the spherical components $m_{\mu\nu}$ of multipole moments. It was shown in [10] that, in the two-particle approximation, the connection between the induced multipole moment $m_{\mu\nu}^{(1I)}$ of the first particle and the spontaneous multipole moment $m_{\mu\nu}^{(2s)}$ of the second one is determined by the relation:

$$m_{\mu\nu}^{(1I)} = -\frac{\mu(\tilde{\varepsilon} - 1)}{\tilde{\mu}\tilde{\varepsilon} + \mu + 1} A_{\mu\nu\lambda\sigma} m_{\lambda\sigma}^{(2s)} + \dots,$$

where the coefficients $A_{\mu\nu\lambda\sigma}$ are given in [12], and

$$m_{\mu,-\nu} = (-1)^\nu m_{\mu\nu}^*, \quad m_{\mu\nu} = m_{\mu\nu}^{(s)} + m_{\mu\nu}^{(I)}.$$

The FMM-contributions to the interparticle potential $U(r)$ are determined by the series

$$U_F(r) = \langle W_{11} \rangle + \langle W_{12} \rangle + \langle W_{13} \rangle + \langle W_{22} \rangle + \dots, \quad (13)$$

where W_{ik} describe the interaction of the i th order multipole for the first particle with the k th order multipole for the second one. The angular brackets in (13) denote the averaging over the distribution of multipole moments. Each term in (13) generates four nonzero contributions caused by their spontaneous and induced multipole moments. For example,

$$\langle m_{10}^{(1)} m_{10}^{(2)} \rangle = \langle m_{10}^{(s1)} m_{10}^{(s2)} \rangle + \langle m_{10}^{(s1)} m_{10}^{(I2)} \rangle + \langle m_{10}^{(I1)} m_{10}^{(s2)} \rangle + \langle m_{10}^{(I1)} m_{10}^{(I2)} \rangle.$$

The contribution $\langle m_{10}^{(I1)} m_{10}^{(I2)} \rangle$ can be omitted as a term of higher order of magnitude.

One can show that the leading terms of the multipole expansion for $U_F(r)$ have the structure:

$$U_F(R) = -\frac{1}{\pi\varepsilon_1} \frac{(\tilde{\varepsilon} - 1)}{(\tilde{\varepsilon} + 2)} \left[9 \frac{r_0^3}{r^6} \langle (m_{10}^{(s)})^2 \rangle + \frac{75}{2} \frac{r_0^3}{r^8} \langle (m_{20}^{(I)})^2 \rangle + 98 \frac{r_0^3}{r^{10}} \langle (m_{30}^{(s)})^2 \rangle + \dots \right]. \quad (14)$$

Here, it is necessary to make the following important remark. The typical life time τ_H of an H-bond is about $(10^{-12} \div 10^{-11})$ s [13]. This time is also characteristic of the variations of \vec{d}_s , so the values of the dielectric permittivities ε_1 and ε_2 should be taken at the frequency $\omega_H \sim \frac{1}{\tau_H}$, for which $\varepsilon_1(\omega_H), \varepsilon_2(\omega_H) \geq 1$. At the same time, the character of the inequality $\varepsilon_2 < \varepsilon_1$ is not violated.

4. Temperature Dependence of k_D

To explain the temperature dependence of the coefficient k_D , we take into account that: 1) the behavior of the mobility g is determined by the effective shear viscosity (5) and 2) the parameter a in the van der Waals equation (3) becomes strongly dependent on temperature due to the FMM-interaction.

Due to the first assumption [see (5)], we can write

$$\frac{g(\Phi)}{g(0)} = 1 + O(\Phi^2),$$

since, in accordance with Section 2, the effective shear viscosity does not include the contribution linear in Φ . The strong temperature dependence of a follows immediately from its definition [14]:

$$a = -2\pi k_B T \int_{2r_0}^{\infty} (1 - e^{-\frac{U(r)}{k_B T}}) r^2 dr \simeq -2\pi \int_{2r_0}^{\infty} U(r) r^2 dr. \quad (15)$$

Substituting to (15)

$$U(r) = U_w(r) + U_F(r),$$

where $U_w(r)$ is the van der Waals attractive potential, we obtain

$$a = a_w - a_F, \quad (16)$$

where

$$a_w = -2\pi \int_{2r_0}^{\infty} U_w(r) r^2 dr > 0$$

and

$$a_F = 2\pi \int_{2r_0}^{\infty} U_F(r) r^2 dr > 0. \quad (17)$$

In accordance with this, the temperature dependence of k_D is described by the expression

$$k_D = \frac{2}{v_m} \left[v_0 + \frac{a_F - a_w}{k_B T} \right]$$

or

$$k_D = 8 \left[1 + \frac{1}{4} \frac{a_F - a_w}{k_B T v_m} \right] \quad (18)$$

if v_0 is approximated by the formula $v_0 = 4v_m$.

For the sake of simplicity, we approximate $U_F(r)$ by its leading term (12). Since $\tilde{\varepsilon} < 1$ and $\varepsilon_1(\omega_H) \sim 1$, expression (12) can be rewritten as

$$U_F(r) \approx \frac{\langle (\vec{d}^{(s)})^2 \rangle}{r_0^3} \left(\frac{r_0}{r} \right)^6. \quad (19)$$

The vector $\vec{d}^{(s)}$ can be approximated by a sum of dipole moments of water molecules entering the monomolecular layer around a trehalose molecule. Therefore, it is convenient to write

$$\langle \vec{d}_s^2 \rangle = \xi^2 d_w^2$$

where d_w is a value of the dipole moment of a water molecule. It follows from the last relation, (17), and (19) that

$$a_F \approx \frac{1}{4} \xi^2 d_w^2$$

and

$$\frac{a_F}{4k_B T v_m} \approx b \frac{T_m}{T}, \quad (20)$$

where

$$b \approx \xi^2 \frac{d_w^2}{16k_B T_m v_m}$$

and T_m is the melting temperature of water.

It is natural to expect that the value of ξ^2 together with $\langle (\vec{d}^{(s)})^2 \rangle$ will be a strongly increasing function of temperature. The more detailed conclusions about them can be made only within the model representations.

With the help of (20), formula (19) takes the form

$$k_D = 8 \left[1 - \frac{T_v}{T} + b \frac{T_m}{T} \right],$$

where $T_v = \frac{a_w}{4k_B v_m}$. In accordance with [15], $d_w \sim 1.85D$. Putting $v_m = \frac{4\pi}{3} r_0^3$ and $r_0 = 0.6 \cdot 10^{-7}$ cm, we obtain

$$b(T) = 0.006 \xi^2(T).$$

The numerical values of $\xi(T)$ allowing to fit experimental data on $k_D(T)$ are given in Table 2. The value of $T_v = 470$ K is got in the self-consistent way. Note that this value of T_v is close to the melting temperature of trehalose.

Table 2. Temperature dependences of parameters b and ξ

T , K	b	ξ
313	0.08	3.6
333	1.25	14.4
358	2.25	19.3

As seen, at enough high temperatures, the values of $\xi(T)$ and ζ_H are of the same order of magnitude. It is an important argument in the favor of the interpretation proposed. The strong temperature dependence of $\xi(T)$ correlates with one for properties of the H-bond network in water. In addition, the identical variation of a and ξ with temperature testifies to the self-consistency of our approach. The estimates for $\xi(T)$ can be partly reduced if the quadrupole-quadrupole interactions and ones of higher orders [see (14)] are taken into account.

Conclusion

The main attention in the present paper is focused on the temperature dependence of the diffusion coefficient in dilute water-trehalose solutions. To explain the strong temperature dependence of the coefficient k_D in (1), we assume, that it is explained by the fluctuation — multipole interaction between admixture particles. Here, the dipole-dipole interaction plays the leading role. It was shown that, due to the relation $\varepsilon_2 < \varepsilon_1$, the interaction between admixture particles has the repulsive character. The higher the temperature, the more is the repulsion. This effect is tightly connected with the variation of stability of the H-bond network in water. Another important circumstance is that the behavior of the diffusion coefficient is determined by the effective shear viscosity. It is essential that the effective shear viscosity of the solution is determined at small φ , the volume fraction of trehalose molecules, by the shear viscosity of a solvent (water).

It was shown that the average number of H-bonds broken in the near surface layer of admixture particles changes from about 4 at the melting point up to 20 at $T = 358$ K. This estimate agrees with one obtained on the basis of geometric reasons [see (4)]. It means that the H-bond network of water is destroyed practically in a monomolecular layer around an admixture particle. This conclusion is in agreement with the results of computer experiments [16]. The fine details of the temperature dependence of k_D depend also on the hydration effects. The analysis shows that the hydration number does not exceed 12. This estimate is confirmed by a more careful consideration of the shear viscosity and the self-diffusion coefficient.

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ОСОБЛИВОСТІ ДИФУЗІЙНИХ ПРОЦЕСІВ У ВОДНИХ РОЗЧИНАХ ТРЕХАЛОЗИ

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Резюме

Досліджено температурну залежність коефіцієнта дифузії D домішкових молекул у розведених водних розчинах трехалози. Показано, що особливості цієї залежності пов'язані, головним чином, з руйнуванням сітки водневих зв'язків у тонкому шарі води, що оточує домішкові частинки, і появою нового внеску в потенціал їхньої взаємодії. В результаті цього потенціал взаємодії змінює свій знак при зростанні температури: з додатного перетворюється на від'ємний. Послідовно враховуються всі суттєві фактори, що впливають на температурну залежність коефіцієнта дифузії.