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Diffusion in water – trehalose solutions

The model of volume fraction dependence of the diffusion coefficient of trehalose molecules in water solution is performed. Two factors influence the diffusion coefficient: the osmotic pressure of trehalose molecules in solution and their mobility. At small values of volume fraction pressure plays the main role, at large enough the mobility does. Due to such concept we managed to explain the surprising behavior of experimentally observed diffusion coefficient.

1. Introduction. In last decades the considerable attention is paid to the study of transport processes in water – trehalose solutions [1 – 3]. In the first place it is connected with studying the bio – protector function of trehalose [1]. This property of trehalose and also others disaccharides remain to be weakly investigated and therefore stimulate the detailed analysis of transport processes and hydration effects in their water solutions. From another side, diffusion coefficient D dependence on volume fraction φ shows a surprising behavior, which has no explanation within the simplest representations of the diffusion process and is the challenge from theoretical point of view.

It was established that at small values of volume fraction ($\varphi < 0.09$) the collective diffusion coefficient increases, attends the maximum at $\varphi = 0.1$ and after this it rapidly decreases. Similar behavior of the diffusion coefficient is observed in other disaccharide solutions too. Two problems arise: 1) theoretical model for such behavior is to be proposed; 2) so small values of the maximum peak position have to be explained.

In previous work [4] we explained the the behavior peculiarities of tangent of inclined angle of $D(\varphi)$ dependence at small values of volume fraction ($\varphi \rightarrow 0$) which are mainly connected with the destruction of the water H – bond network in thin layer around trehalose molecule and appearance of new contribution to the inter – molecular potential.

In this paper $D(\varphi)$ dependence in all range of experimentally observed volume fraction ($0 < \varphi < 0.4$) performed and curiously small value of peak position explained using the knowledge of H – bonds and interaction potential [4].

2. General structure of the diffusion coefficient. In general case, for solid spherical particles, the volume fraction φ dependence of the collective diffusion coefficient on the measured experimentally φ is represented as follows

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

where $D(0)$ – is the diffusion coefficient for infinitely dilute solution, $g(\varphi)$ – is the mobility of the particle, $P(n)$ – osmotic pressure considered as a function of density n of admixture particles, T – is temperature.

The volume fraction φ (used in [2, 3] for the description of experimental data)

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

is a volume fraction of ideal solution. 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, ρ_t and ρ_w are the mass densities of trehalose melt and pure water.

Due to hydration effects the real volume fraction Φ , occupied by admixture particles (trehalose molecule with mono layer of hydrated water molecules), is more than φ and can be determined by the relation

$$\Phi = \frac{\left(\frac{M_t}{\rho_t} + \frac{M_w}{\rho_w} n_H \right) n_t}{\frac{M_t n_t}{\rho_t} + \frac{M_w n_w}{\rho_w}}, \quad (2)$$

where n_H is the hydration number of water molecules (jointed with a trehalose molecule). It is not difficult to see, that:

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

At $\rho_t \cong \rho_w$, previous formula can be rewritten in the form:

$$\Phi = \left(1 + \frac{M_w}{M_t} n_H \right) \varphi, \quad (3)$$

where $\frac{M_w}{M_t} = 0.053$ is the ratio of molecular masses for water (M_w) and a trehalose molecule (M_t).

3. The osmotic pressure. The osmotic pressure of admixture particles can be modeled by the virial expansion

$$P = nk_B T (1 + nv_0 + (nv_0)^2 + \dots) - an^2, \quad (4)$$

where $v_0 = 4v_m$, and $v_m = \frac{4}{3}\pi r_0^3$ is the molecular volume, r_0 radius of trehalose molecule.

In general [5], the coefficient a is connected with interparticle potential $U(r)$ by the relation

Table. Temperature dependence of the parameter ξ [4].

T, K	313	333	358
ξ	3.6	14.4	19.3

$$a = -2\pi k_B T \int_{2r_0}^{\infty} \left(1 - e^{-\frac{U(r)}{k_B T}}\right) r^2 dr \cong -2\pi \int_{2r_0}^{\infty} U(r) r^2 dr. \quad (5)$$

As it's been shown in [4] the potential $U(r)$ is the sum of the Van der Waals contribution $U_w(r)$ and the term $U_F(r)$ caused by the fluctuation multipole interactions [6]

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

In fact, both terms U_w and U_F are originated by fluctuations of the electric field, however, U_w is connected with high frequency ones in the electronic cells of molecule, while U_F arises due to the destruction of the H-bond network in water around a trehalose molecule the last acquires the nonzero dipole moment, as a result, the additional fluctuation multipole-multipole potential of intermolecular interaction arises [4]:

$$U_F(r) = \frac{\langle (\overset{\bullet}{d}_s)^2 \rangle}{r_0^3} \left(\frac{r_0}{r}\right)^6. \quad (6)$$

Here d_s is the fluctuational dipole moment of an admixture molecule. More exactly $\overset{\bullet}{d}_s$ is the sum of dipole moments of water molecules, forming the molecular layer around a trehalose molecule. It is expedient to write $\langle d_s^2 \rangle = \xi^2 d_w^2$, where d_w is the dipole moment of a water molecule. So the number of water molecules in the shell which surrounds the trehalose molecule and generates dipole moment of complex molecule is equal to ξ . As a result

$$a = a_w - a_F, \quad a_F = \frac{1}{4} \xi^2 d_w^2, \quad a_w = \frac{11}{4} k_B T_0 v_m, \quad (7)$$

$T_0 = 470K$ for this system [4]. It is naturally to expect that ξ and also $\langle (\overset{\bullet}{d}_s)^2 \rangle$ are strong functions of temperature. Values of ξ at different temperatures were obtained in [4] and placed in Table.

It was shown [4] that the average number of water molecules, hydrated by a trehalose molecule equals to $n_H \approx 14$. As we can see, the values of $\xi(T)$ and n_H are of the same order of magnitude. This is important argument in favor of interpretation proposed. The strong temperature dependence of ξ is in agreement with the tendency, characteristic for H-bond networks of water [2,3] in the investigated temperature interval. Therefore, the similar variations of a and ξ with temperature testify on the self – consistency of the approach proposed. The estimates for $\xi(T)$ can be improved if we take into account the quadrupole – quadrupole interactions and ones of higher order in the formula (6).

4. The effective shear viscosity. The values of the shear viscosity depend on the experimental methods used for its measuring. This statement naturally illustrates by the motion of Brownian particle with radius R_b in suspension of hard spheres with radius R_0 . Evidently that thermal motion of a Brownian particle depends on its size R_b and the average distance between suspended particles R_G . It is necessary to differ the following characteristic cases:

$$1) R_b \leq R_0 \ll R_G, \quad 2) R_b \leq R_0 \ll R, \quad 3) R_b \gg R_G.$$

In the first case when the size of a Brownian particle is essentially smaller R_G , its mobility g is mainly determined by the shear viscosity η_0 of the solvent. It is so, since suspended particles play the role of far boundary, almost not influencing the character of hydrodynamic flows in the vicinity of Brownian particles. Unlike this in the third case, when $R_b \gg R_G$, the mobility of a particle is inversely proportional to the average shear viscosity $\bar{\eta}$. In more direct way these values of the shear viscosity are measured in the viscosimetric experiments.

In the intermediate case when $R_b \leq R_0 \leq R_G$, the mutual disposition of admixture particles considerably influence its mobility, which should be proportional to so called effective shear viscosity η_{eff} . The magnitude of η_{eff} is more than η_0 , but smaller than $\bar{\eta}$.

In particular, the value of η_{eff} can be obtained from NMR measurements, since the self-diffusion coefficient D_s of dense enough system is inversely proportional namely the effective shear viscosity.

It was proposed [8] a new version of the cell model for the determination of the average and effective shear viscosities for suspension of hard spheres. According to [8], the expression for the effective shear viscosity takes the following form

$$\eta_{eff} = \eta_0 \frac{1 - \psi}{2 - \psi - \sqrt{1 - 2\psi^2(1 - \psi)}} = \eta_0 F(\Phi), \quad (8)$$

where $\psi = \frac{6}{\pi} \frac{\Phi}{(0.93 + 0.127\Phi)^3}$.

At $\Phi \rightarrow 0$ the formula (8) has the asymptote

$$\eta_{eff}(\Phi) = \eta_0(1 + 6.25\Phi^2 + \dots). \quad (9)$$

The comparison of the effective η_{eff} and average shear viscosities is presented in Fig. 1.

5. The diffusion coefficient. We take into account that the behavior of the mobility g is determined with the effective shear viscosity

$$\frac{g(\Phi)}{g_0} = \frac{\eta_{eff}(0)}{\eta_{eff}(\Phi)} = F(\Phi). \quad (10)$$

As it follows from formula (1), that the volume fraction dependence of the diffusion coefficient is determined by two factors: 1) osmotic pressure, leading to increase

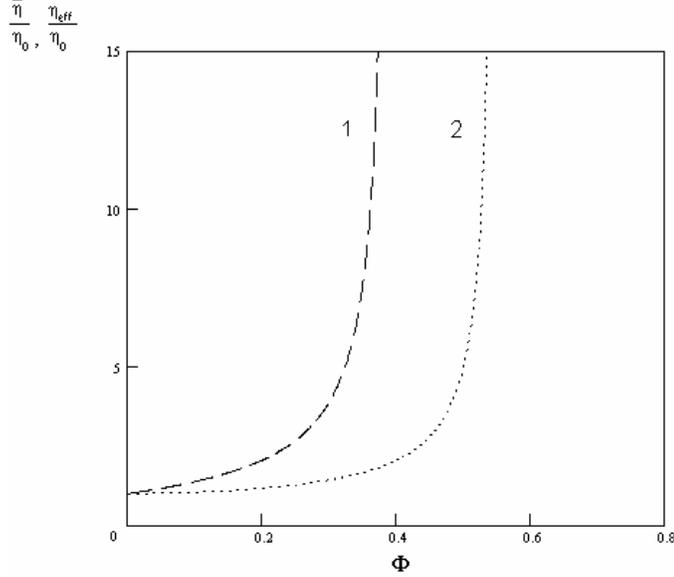


Fig. 1. Volume fraction dependence of the average (the curve 1) and effective (2) shear viscosities.

of D with Φ and 2) the effective shear viscosity of surrounding liquid, which reduces the diffusion coefficient when Φ increases. From (4) we find

$$\frac{\partial P}{\partial n} = k_B T \left(1 + 2v_0 \left[1 - \frac{a}{k_B T v_0} \right] n \right) = k_B T \left(1 + 8\Phi \left[1 - \frac{a}{4k_B T v_m} \right] \right), \quad (11)$$

where a is defined in (5). And finely the expression for the diffusion coefficient in all range of volume fraction values has a form

$$D(\Phi) = D(0)F(\Phi) \left(1 + 8\Phi \left[1 - \frac{a}{4k_B T v_m} \right] \right). \quad (12)$$

The reason of the peak existence is: at small values of volume fraction the density derivative of pressure is proportional to Φ

$$\frac{\partial P(n)}{\partial n} \sim \Phi \quad \text{and} \quad \eta_{eff} = \eta_0(1 + 6.25\Phi^2 \dots)$$

the effective shear viscosity changes as the square of Φ , therefore the behavior of the diffusion coefficient is determined by the osmotic pressure: D increases. At large values of Φ the effective shear viscosity has the dominate influence, that leads to the reduction of D .

6. Peculiarities of the diffusion process in water – trehalose solution.

The analysis of the formula (12) allows concluding, that the position of maximum of $D(\Phi)$ for hard spheres corresponds to $\Phi \approx 0.4$. This value of the volume fraction is four times more than the value measured in experiments for trehalose – water solution. It was noticed [2, 3] that the hydration phenomenon strongly influences transport processes in water – trehalose solution. Let us consider this effect in more details.

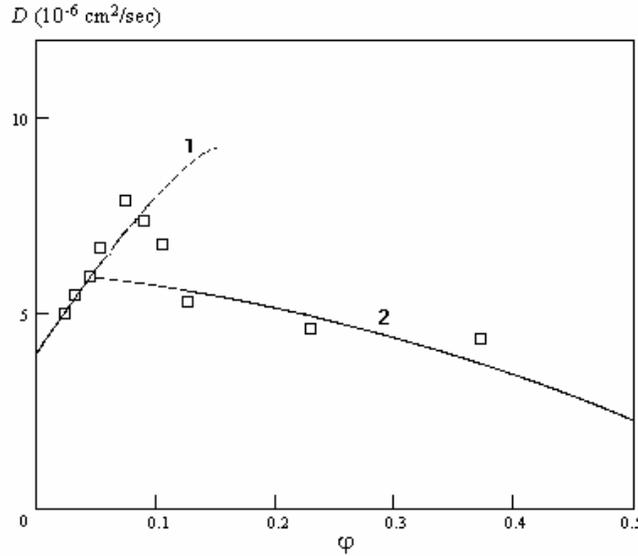


Fig. 2. Volume fraction dependence of the diffusion coefficient of trehalose molecule: the curve 1 corresponds to the formula (1), 2 – the formula (12), squares – to experimental data [3].

At small enough values of the volume fraction the hydrated shell of two neighbor trehalose molecules does not overlap. When volume fraction increases, this condition becomes violated and consequently a trehalose molecule with its hydrated shell can not be considered as an isolated complex particle (trehalose molecule + hydrated water molecule). As a result, the Van der Waals expression for the osmotic pressure is not applicable.

Let us estimate the applicability region for the formula (4). One supposes that the density derivative of pressure tends to zero when molecular complexes form spatial percolation configuration. For such system of spherical particles the percolation barrier is equal to $\Phi_* \approx 0.3$. Since the geometrical radius of a trehalose molecule equals to 6 \AA the thickness of hydration shell is about 3 \AA , we obtain that the radius $\%_0$ of a molecule and its molecular complex equals to 9 \AA . From here it follows that the ratio $\frac{\%_0}{r_0}$ of radiuses of a complex particle and a trehalose molecule is equal to 1.5.

Since volume of a trehalose molecule and its molecular complex is proportional to $\%_0^3$, the volume fraction φ_m , measured experimentally for the percolation configuration and Φ_* are connected by (with) the following relation:

$$\frac{\Phi_*}{\varphi_m} = \left(\frac{\%_0}{r_0} \right)^3 \quad \text{hence} \quad \varphi_m = \Phi_* \left(\frac{r_0}{\%_0} \right)^3. \quad (13)$$

From (13) it follows that $\varphi_m = 0.09$. This estimation for the applicability region of our theory coincides with the experimental values of volume fraction, at which the diffusion coefficient reaches maximum. Up to $\varphi_m = 0.09$ it is possible to use representation (4) (curve 1 in Fig.2). At $\varphi > \varphi_m$ the Van der Waals equation of state is not

applicable, since the density derivative of the osmotic pressure becomes negative. In this region the mobility of a complex particle plays the main role. Therefore equation (12) should be written in the form

$$D(\varphi) = \frac{D(0)A}{k_B T} \frac{g(\varphi)}{g(0)}, \quad (14)$$

where constant A is equal to the density derivative of osmotic pressure at $\varphi = \varphi_m$:

$$A = \left. \frac{\partial P}{\partial n} \right|_{\varphi = \varphi_m}.$$

The comparison of values for the diffusion coefficient, calculated according to (14), with experimental data is represented with the curve 2 (Fig. 2).

7. Conclusion.

The main attention in the present paper is focused on the volume fraction dependence of the diffusion coefficient in dilute water-trehalose solutions. The main feature of the behavior of diffusion coefficient in this system is the small enough peak volume fraction value. It was shown that such small value is due to the effect of overlapping of the trehalose molecules hydrated shells. The theory at small and large volume fraction values is proposed. The comparison with experimental data is performed.

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Дифузія у водних розчинах трехалози

АНОТАЦІЯ

Запропонована модель залежності коефіцієнта дифузії молекул трехалози від їх об'ємної частки у водному розчині. Два фактори впливають на коефіцієнт дифузії: осмотичний тиск молекул трехалози в розчиннику та їх рухливість. При малих значеннях об'ємної долі основну роль грає осмотичний тиск, а при великих – рухливість. Завдяки таким припущенням можна пояснити доволі незвичну поведінку коефіцієнта дифузії, яка спостерігається експериментально.

Орлов Е.В.

Диффузия в водных растворах трехалозы

АННОТАЦИЯ

Предложена модель зависимости коэффициента диффузии молекул трехалозы от их объемной доли в водном растворе. Два фактора влияют на коэффициент диффузии: осмотическое давление молекул трехалозы в растворителе и их подвижность. При малых значениях объемной доли основную роль играет осмотическое давление, а при больших – подвижность. Благодаря таким допущениям можно объяснить довольно необычное поведение коэффициента диффузии, наблюдаемое экспериментально.