APPLICATION OF VISCOSIMETRIC METHOD TO STUDY CONFIGURATIONAL TRANSITIONS IN GLUCOSE AQUEOUS SOLUTIONS

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The shear viscosity has been measured for glucose aqueous solutions in the concentration range of 12.5–100 g/l and the temperature interval of 293–353 K. Experimental data are interpreted on the basis of Einstein's theoretical model. The fractions of glucose molecules in the "chair" and "boat" configurations are determined at various temperatures. The thermodynamic parameters that characterize the "chair"–"boat" configurational transition of a glucose molecule are evaluated. The numbers of water molecules in the hydration shells of both configurations were found. The "chair"–"boat" configurational transition is shown to result in the almost complete destruction of the hydration shell of a glucose molecule. The bonds of a glucose molecule in the "chair" configuration are found to be deformed, and the corresponding deformation energy is evaluated.

1. Introduction

Much attention was drawn to the research of aqueous solutions of glucose [1, 2]. It is associated, first of all, with a wide application of those solutions in medicine. It is known [3] that glucose $C_6H_{12}O_6$ belongs to the monosaccharide class. In solutions, the carbon atoms of a glucose molecule form a ring; it is the so-called gluco-pyranose cycle.

By definition [4], the term "molecular configuration" means a certain arrangement of atoms, which constitute the molecule, in the space. Accordingly, to describe the configuration of a molecule, it is necessary to know the coordinates of all its atoms. Since the latter interact with one another, every configuration is characterized by a definite value of potential energy. For some configurations, the potential energy is minimal. These configurations are called relatively stable. For a glucose molecule, the configurations are distinguished according to two attributes [3]. The first attribute is the arrangement of carbon atoms. From this point of view, the "boat" configuration (Fig. 1) and the "chair" one (Fig. 2) turn out the most stable for the glucose molecule. The second attribute used to distinguish between relatively stable configurations of the molecule is the arrangement of the so-called hemiacetal hydroxyl group (it is encircled in Figs. 3 and 4). There are two such configurations: the α-form, in which the hemiacetal hydroxyl group is oriented as the majority of other hydroxyl groups (Fig. 3); and the β-form, in which it is oriented oppositely (Fig. 4). Owing to thermal fluctuations, transitions between the relatively stable molecular configurations take place; they are called configurational transitions.

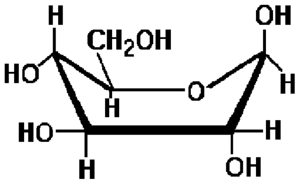

Fig. 1. The "boat" configuration of a glucose molecule

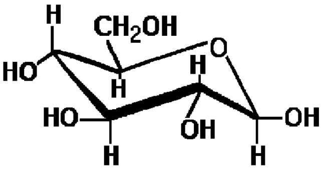

Fig. 2. The "chair" configuration of a glucose molecule

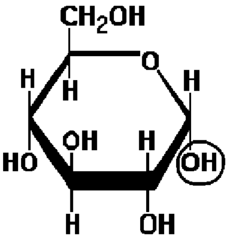

Fig. 3. The α-form of a glucose molecule

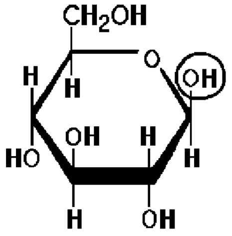

Fig. 4. The β-form of a glucose molecule

In this work, we applied the viscosimetric method to study the configurational transitions in the glucose molecule. The aim of the work was to determine the fraction of glucose molecules in either configuration using the experimental data on the viscosity of aqueous solutions of glucose.

2. Experimental Technique and Results Obtained

The experiment was carried out with the use of a capillary viscometer described in work [5]. The kinematic viscosity ν of aqueous solutions of glucose with various concentrations c was measured in the temperature interval of 293–353 K. The results obtained are depicted in Fig. 5.

3. Discussion of Experimental Results

In works [6, 7], the molecular size of a dissolved substance was proposed to be determined by measuring the shear viscosity of its solution. Molecules of a solute were considered as hard spheres, and the solvent as a continuous medium. The following formula was obtained for the shear viscosity of the solution [6]:

$$\eta = \eta_0 \left(1 + \frac{5}{2}\frac{4\pi R^3}{3} n\right), \tag{1}$$

where η_0 is the shear viscosity of the solvent, and R is the radius of the model hard sphere or, according to A. Einstein, the effective hydrodynamic radius of a molecule.

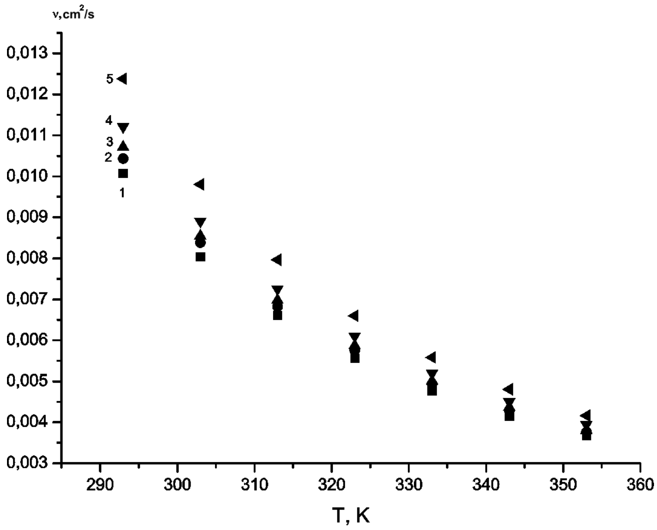

Fig. 5. Temperature dependences of the kinematic viscosity of glucose aqueous solutions with the glucose concentrations: 0 (*1*), 12.5 (*2*), 25 (*3*), 50 (*4*), and 100 g/l (*5*)

In his work [6], A. Einstein emphasized that this model can be used, if the solute molecule dimension exceeds substantially that of the solvent molecule. In the same work, experimental data on the viscosity of sucrose aqueous solutions were analyzed on the basis of the model proposed. In other words, A. Einstein adopted that the sucrose molecule satisfied the criterion formulated above for the model to be applicable.

The sucrose molecule consists of two linked glucopyranose cycles [3]. The glucose molecule, as was already mentioned, includes one such cycle. Therefore, its radius of inertia should not differ considerably from that of sucrose molecule. This circumstance allows us to hope that the application of Einstein's model to glucose aqueous solutions is eligible.

Using formula (1) and the experimental data exhibited in Fig. 5, we calculated the effective hydrodynamic radius of a glucose molecule at various temperatures. The results of calculations are presented in Fig. 6. The figure demonstrates that the effective hydrodynamic radius of a glucose molecule changes with the temperature. To explain this phenomenon, let us assume that the glucose molecule can exist in two configurations with effective hydrodynamic radii R_1 and R_2. This means that there are two sorts of model spheres in the solvent simultaneously, and the quantity R^3 in formula (1) is averaged, being defined by the formula

$$R^3 = R_1^3 w_1 + R_2^3 w_2, \tag{2}$$

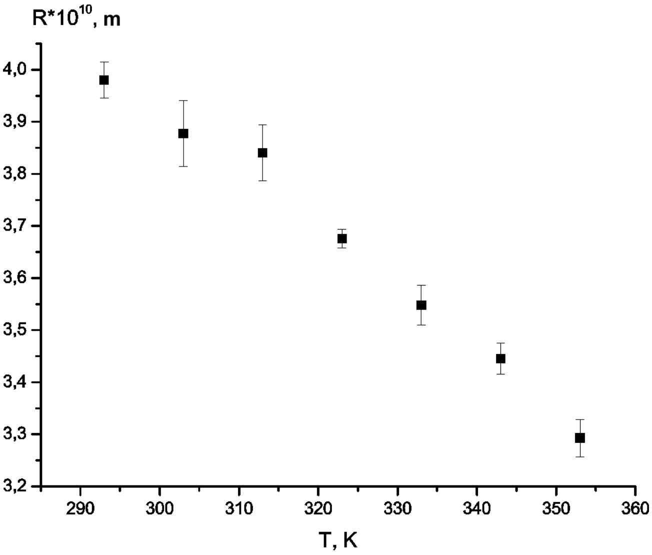

Fig. 6. Temperature dependence of the effective hydrodynamic radius of a glucose molecule in the interval of (293–353) K

where w_1 and w_2 are the probabilities for the corresponding configurations, for which the equality

$$w_1 + w_2 = 1. \tag{3}$$

is satisfied. As follows from formulas (1) and (2), the viscosimetric experiment can distinguish between configurations only if the corresponding effective hydrodynamic radii are different. Even without calculations, but on the basis of Figs. 3 and 4, a conclusion can be drawn that the inertia radii and, hence, the effective hydrodynamic radii are almost identical for the α- and β-forms. On the contrary, as one can see from Figs. 1 and 2, the inertia radii of "chair" and "boat" configurations are different, with the inertia radius of the former being larger. Hence, the viscosimetric experiment "does not see" the difference between the α- and β-forms, so that formula (3) regards the "chair" and "boat" configurations. Let the notations R_1 and R_2 be related to the former and the latter configuration, respectively.

In the framework of the model concerned, the temperature dependence of R can be explained only if we admit that the ratio between the numbers of molecules in the "chair" and "boat" configurations changes with the temperature, or, in other words, that the probabilities w_1 and w_2 are temperature-dependent.

In the solution, the glucose molecule interacts with its environment, which mainly consists of water molecules. Therefore, the configurational transitions, which are dealt with in this work, are accompanied by changes in the environment. Let us draw a spherical surface around a glucose molecule; the center of the sphere coincides with the center of mass of the molecule. Let the environment structure vary inside a sphere of radius L. Below, the sphere of such a dimension will be referred to as a subsystem. Then, a certain equilibrium state of the subsystem corresponds to each of the two considered relatively stable configurations of the glucose molecule. Such states are traditionally called the states of local equilibrium [8], and the very subsystem, in which the mentioned states are established, is called the physically infinitesimal volume [8, 9]. In what follows, the states of local equilibrium are referred to as states.

Hence, we deal with a subsystem that can exist in two states. Let F_1 and F_2 denote their free energies. Again, let us introduce the notation $\Delta F = F_2 - F_1$. According to the thermodynamic theory of fluctuations [10],

$$w_2/w_1 = \exp\left(-\frac{\Delta F}{k_\mathrm{B}T}\right), \tag{4}$$

where k_B is the Boltzmann constant. Then, taking formula (3) into account, the probabilities for the states with the free energies F_1 and F_2 are

$$w_1 = \frac{1}{1+\exp(-\Delta F/k_\mathrm{B}T)}, \tag{5}$$

$$w_2 = \frac{\exp(-\Delta F/k_\mathrm{B}T)}{1+\exp(-\Delta F/k_\mathrm{B}T)}. \tag{6}$$

Let us write down the known expressions

$$F_1 = U_1 - TS_1, \tag{7}$$

$$F_2 = U_2 - TS_2 \tag{8}$$

for the free energies. Here, U_1 and U_2 are the energies, and S_1 and S_2 the entropies of the corresponding states. Let us introduce the notations $\Delta U = U_2 - U_1$ and $\Delta S = S_2 - S_1$. We rewrite formulas (5) and (6) as follows:

$$w_1 = \frac{1}{1+\exp(\Delta S/k_\mathrm{B})\exp(-\Delta U/k_\mathrm{B}T)}, \tag{9}$$

$$w_2 = \frac{\exp(\Delta S/k_\mathrm{B})\exp(-\Delta U/k_\mathrm{B}T)}{1+\exp(\Delta S/k_\mathrm{B})\exp(-\Delta U/k_\mathrm{B}T)}. \tag{10}$$

Substituting equalities (9) and (10) into formula (2), we obtain

$$R^3 = R_1^3\frac{1}{1+\exp(\Delta S/k_\mathrm{B})\exp(-\Delta U/k_\mathrm{B}T)}+$$

$$+R_2^3\frac{\exp(\Delta S/k_\mathrm{B})\exp(-\Delta U/k_\mathrm{B}T)}{1+\exp(\Delta S/k_\mathrm{B})\exp(-\Delta U/k_\mathrm{B}T)}. \tag{11}$$

Using the least square method, we approximated the experimental temperature dependence of the effective hydrodynamic radius of a glucose molecule by formula (11) to find the unknown quantities R_1, R_2, ΔU, and ΔS. Their corresponding values are given in Table 1.

The data in Table 1 allow us, first of all, to determine the probabilities to find a glucose molecule in the "chair" and "boat" configurations. Using formulas (9) and (10), as well as ΔU- and ΔS-values from Table 1, we obtain the temperature dependences $w_1(T)$ and $w_2(T)$ (see Fig. 7).

We can also determine the concentrations of molecules in the "chair" and "boat" configurations. Let those concentrations be designated as c_1 and c_2, respectively. The following equalities are obvious:

$$c_1 = cw_1, \tag{12}$$

$$c_2 = cw_2. \tag{13}$$

In addition, we are able to estimate the changes in the aqueous environment of a glucose molecule. For this purpose, using the known data [11] on the spatial arrangement of atoms in a glucose molecule in both mentioned configurations, let us calculate the corresponding radii of inertia r_1 and r_2. The results of this calculation are $r_1 = 2.45$ Å and $r_2 = 2.29$ Å. It is less than the corresponding values of effective hydrodynamic radii R_1 and R_2 obtained from the experiment (Table 1). This fact brings us to a conclusion that water molecules, which are located in a layer of the thickness $h_1 = R_1 - r_1$ in the case of "chair" configuration and of the thickness $h_2 = R_2 - r_2$ in the case of "boat" configuration, move with the glucose molecule as a unit. In other words, the quantities h_1 and h_2 are the thicknesses of hydration spheres for the corresponding configurations.

Let us estimate the number of water molecules that move together with a glucose molecule as a unit. In his work [6], A. Einstein called this water bound. It is the molecules of bound water that form the hydration sphere. Let the corresponding numbers be q_1 for the "chair" and q_2 for the "boat" configuration. Dividing the volumes of hydration spheres by the volume v of a water molecule, we obtain

T a b l e 1. Thermodynamic parameters of the configurational transition of a glucose molecule

Effective hydrodynamic radii		Energy increment at the configurational transition	Entropy increment at the configurational transition
R_1, Å	R_2, Å	ΔU, J	ΔS
4.11	2.65	4300	12.4 k_B

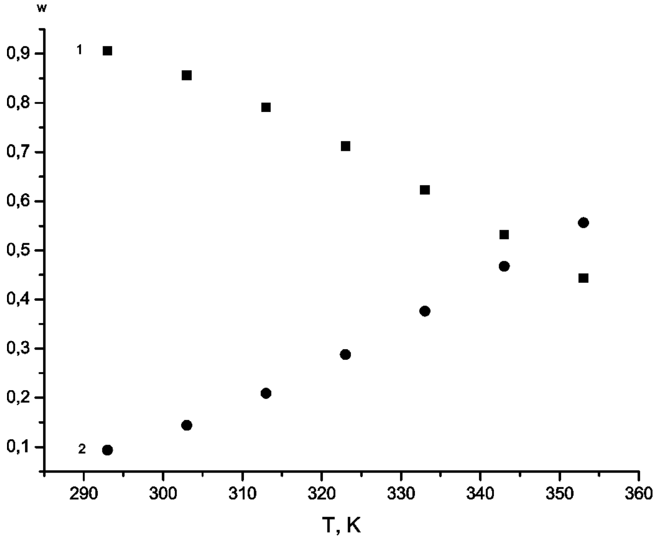

Fig. 7. Probabilities to find glucose molecules in the "chair" (*1*) and "boat" (*2*) configurations

$$q_1 = \frac{1}{v}\frac{4\pi}{3}\left(R_1^3 - r_1^3\right), \tag{14}$$

$$q_2 = \frac{1}{v}\frac{4\pi}{3}\left(R_2^3 - r_2^3\right), \tag{15}$$

The numbers of water molecules coupled with a glucose molecule in the corresponding configurations, which were calculated by those formulas, are quoted in Table 2. It is worth emphasizing that these values were obtained under the assumption that the form of a glucose molecule can be represented as a sphere. Therefore, they should be considered as an estimation of the corresponding values. However, even these estimations allow us to draw a conclusion that the hydration sphere of a glucose molecule becomes almost completely destroyed at the transition from the "chair" to the "boat" configuration.

Another argument in favor of this conclusion is a considerable growth of the entropy (Table 1) at the "chair" → "boat" transition, which testifies to a substantial disordering in the system at this transition.

Using the value of entropy increment ΔS, let us find the size of the physically infinitesimal volume inherent to the configurational transition concerned. In other words, let us estimate the extension of the region, which, surrounding a glucose molecule, perceives the existence of this transition. By its dimensions, it is bigger than the hydration sphere, including the latter as a component.

The estimation will be carried out in the framework of the network liquid model [12]. According to it, the space occupied by the liquid is partitioned into cells. While calculating the thermodynamic characteristics of a liquid, the probabilities to find one, two, and so on molecules in a cell are determined.

Let the cell dimension in the network liquid model be equal to the size of an elementary cell in a lattice, which is formed by molecules in the crystalline phase. In this case, the probability to find two and more molecules in a cell can be neglected. At the same time, there appear a certain number of empty cells in the structure. They are analogs of vacancies in the crystal lattice. However, unlike vacancies, these cavities have irregular shapes, because the molecules surrounding the cavities are not located at the lattice sites.

We neglect this circumstance in our approximate consideration and use the known formula of the solid-state theory to calculate the collective entropy of a liquid S_C [13]:

$$S_C = k_{\mathrm{B}} \ln \frac{N!}{n!(N-n)!}. \qquad (16)$$

In the adopted model of the liquid, the quantities in formula (16) are as follows: N is the total number of cells that the liquid is divided into, and n is the number of cavities in the liquid. The system – or, to be exact, a subsystem concerned – is a physically infinitesimal volume. Therefore, the quantity N, by its meaning, is the number of cells in the aqueous environment of a glucose molecule.

As was already mentioned, the number of water molecules in the hydration shell of glucose molecule decreases by the value $\Delta q = q_1 - q_2$ at the "chair" → "boat" configurational transition. Accordingly, the distances reckoned from the centers of inertia of these molecules to the center of inertia of a glucose molecule increase. In the framework of the adopted model of a liquid, one may suppose that Δq cavities emerge at that, i.e. the quantity Δq can be identified with n in formula (16). In this approach, when the disordering is reduced to the emergence of cavities in a vicinity of the glucose molecule, the entropy increment ΔS must be identified with the collective entropy S_C.

Substituting the determined quantities $n = \Delta q$ and $S_C = \Delta S$ into formula (16), we obtain the value $N \approx 25$. Supposing that the region occupied by the physically infinitesimal volume is a sphere of radius L, we obtain the following formula for the volume of this region:

$$vN = \frac{4\pi}{3}\left(L^3 - r_1^3\right). \qquad (17)$$

The L-value calculated by this formula is given in Table 2.

According to the earlier speculations, there emerge Δq cavities in the glucose molecule environment at the transition "chair" → "boat". The formation of every cavity should be accompanied at least by the destruction of a hydrogen bond. Accordingly, we have the estimate $\Delta U_C \geq \Delta q E$ for an energy increment owing to the transition concerned, where E is the energy of a hydrogen bond. Substituting the value of energy E into this expression, we obtain that the experimental value of ΔU is considerably lower than the calculated one, ΔU_C. This brings us to a conclusion that the bonds that form the "chair" configuration are deformed, and the corresponding energy is of the order of $\Delta U_C - \Delta U \sim 10^4$ K. The "boat" configuration is almost free of those deformations. Bearing in mind that the hydration sphere is practically destroyed for the latter, it is reasonable to suppose that deformations of bonds in the "chair" configuration arise under the action of water molecules that form the hydration sphere.

As is seen from Fig. 6, the temperature dependence of the effective hydrodynamic radius of a glucose molecule has a peculiarity at 313 K. It is known [14] that there is the dynamical phase transition in water at this temperature. Therefore, the observed peculiarity can be associated with the existence of this phase transition. It is also known that this phase transition is accompanied by a reconstruction of the net of hydrogen bonds. Such a reconstruction is surely reflected on the hydration sphere of a glucose molecule. It is this circumstance that is responsible for the observed peculiarity in the temperature dependence of the effective hydrodynamic radius of a glucose molecule.

Table 2. Structural characteristics of the aqueous environment of a glucose molecule

The number of water molecules in the hydrodynamic shell		The number of water molecules in the physically infinitesimal volume (PIV)	The size of physically infinitesimal volume (PIV)
q_1	q_2	N	$2L$, Å
7	1	25	12

4. Conclusions

The application of the viscosimetric method allowed us to determine the number of glucose molecules that are in the “chair” and “boat” configurations in the temperature range of 293 – 353 K. We also obtained the new information concerning the “chair”–“boat” transition of a glucose molecule:
1) in the course of this transition, the hydration sphere of glucose molecule undergoes the destruction; there are seven water molecules in the hydration shell of the “chair” configuration and only one molecule in the shell of the “boat” configuration;
2) in comparison with the bonds in the “boat” configuration, the bonds in the “chair” one are deformed, and their deformation energy is 10^4 K;
3) the “chair” and “boat” configurations correspond to local equilibrium states, which are established in a physically infinitesimal volume about 1.2 nm in dimension; this volume includes a glucose molecule and 25 water molecules.

The observed peculiarity in the temperature dependence of the effective hydrodynamic radius of a glucose molecule at a temperature of 313 K is associated with the existence of a dynamical phase transition in water.

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ЗАСТОСУВАННЯ ВІСКОЗИМЕТРИЧНОГО МЕТОДУ ДЛЯ ВИВЧЕННЯ КОНФІГУРАЦІЙНИХ ПЕРЕХОДІВ У ВОДНИХ РОЗЧИНАХ ГЛЮКОЗИ

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Резюме

Отримано значення зсувної в'язкості водних розчинів глюкози в інтервалі концентрацій 12,5–100 г/л і температур 293–353 К. Інтерпретацію експериментальних даних проведено на основі теоретичної моделі А. Ейнштейна. Визначено кількість молекул глюкози, що знаходяться в конфігураціях “крісло” та “човен” за різних температур. Одержано значення термодинамічних параметрів, які характеризують конфігураційний перехід “крісло–човен” молекули глюкози. Визначено кількості молекул води, що утворюють гідратну оболонку обох вказаних конфігурацій. Показано, що при згаданому переході практично повністю руйнується гідратна оболонка молекули глюкози. Встановлено, що зв'язки молекули глюкози в конфігурації “крісло” деформовані. Одержано оцінку для енергії деформації цих зв'язків.