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Molecular Mechanism of the Viscosity of Aqueous Glucose Solutions

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Abstract—Experimental relations are obtained for the viscosity of aqueous glucose solutions in the temperature range of 10−80°C and concentration range 0.01−2.5%. It is found that the concentration dependence of fluidity is linear when the concentration is higher than a certain value and varies at different temperatures. The existence of such a dependence indicates that the mobilities of solvent and solute molecules are independent of the concentration of solutions. This assumption is used to construct a theoretical model, in which the structure of an aqueous glucose solution is presented as a combination of two weakly interacting networks formed by hydrogen bonds between water molecules and between glucose molecules. Theoretical relations are obtained using this model of network solution structure for the concentration and temperature dependence of solution viscosity. Experimental data are used to calculate the activation energies for water ($U_w = 3.0 \times 10^{-20}$ J) and glucose molecules ($U_g = 2.8 \times 10^{-20}$ J). It is shown that the viscosity of a solution in such a network structure is governed by the Brownian motion of solitons along the chains of hydrogen bonds. The weak interaction between networks results in the contributions to solution fluidity made by the motion of solitons in both of them being almost independent.

INTRODUCTION

The important role played by glucose and its solution in the vital activity of an organism attracts the attention of many researchers. The viscosity of glucose solutions was studied in [1, 2] and a number of other works. In this work, we consider the molecular mechanism of this phenomenon.

When we consider the theory of molecular solution viscosity, it is obvious the main aim of such a theory is to construct a molecular mechanism that would explain the experimentally observed concentration and temperature dependence of solution viscosity. We could not find any solution to this problem in the literature. It is therefore the aim of this work.

Our starting point is the theory of the viscosity of simple liquids [3]. By definition, simple liquids are sets of identical small molecules. According to this theory, the viscosity of such liquids is governed by the Brownian motion (random movement) of molecules. This motion is a sequence of elementary displacements (elementary acts) in which a molecule overcomes a particular energy barrier U.

This theory yields shear viscosity η according to the formula

$$\eta = \frac{1}{\delta q}, \tag{1}$$

where δ is the size of the molecule and q is its mobility, determined as

$$q = \frac{h^2}{2\tau k_B T} \exp\left(-\frac{U}{k_B T}\right), \tag{2}$$

where τ the period of the thermal vibrations of a molecule as a whole, k_B is the Boltzmann constant, T is temperature, and h is the length of an elementary displacement.

In solving the above problem of the concentration and temperature dependence of solution viscosity, we shall basically retain the assumptions of this theory but make two additions to it.

The first addition considers that a liquid system now consists of two kinds of molecules, solvent and solute.

The second addition stems from the theory's assumption [3] that the environment of a molecule is a continuous medium. This assumption contains an obvious contradiction: when the problem is solved at the molecular level and the motion of a certain molecule is considered, the environment of this molecule should logically be considered a set of molecules instead of a continuous medium. We shall try to eliminate this contradiction in our computational model.

THEORETICAL

As is well known, the concept of viscosity is introduced in hydrodynamics (see, e.g., [4]) by the relation

$$\sigma_{xy} = \eta \frac{\partial v_x}{\partial y}, \qquad (3)$$

where v_x is the flow velocity. Equation (3) corresponds to a simple shear in plane xy, and σ_{xy} is the tangential shear stress.

Both stress and velocity are determined in a region referred to as a mathematically infinite small volume. In hydrodynamics based on the continuous medium model, the size of this region is considered to be infinitely small. When the molecular approach is used, a physically infinite small volume (a block with size L) corresponds to a mathematically infinite small volume.

We must therefore replace the differentials of hydrodynamic theory with finite differences:

$$\frac{\partial v_x}{\partial y} = \frac{v_x - v'_x}{y - y'}, \qquad (4)$$

where y and y' are the coordinates of the centers of inertia of neighboring blocks, and v_x and v'_x are the velocities of these blocks as whole units. These velocities are naturally assigned to each block's center of inertia.

As follows from Eq. (4), the transition to finite differences means that we must now consider the relative motion of two neighboring blocks when interpreting the term viscosity. It is obvious that distance $y - y'$ between their centers is equal to size L of the above blocks, allowing us to rewrite Eq. (4) as

$$\frac{\partial v_x}{\partial y} = \frac{v_x - v'_x}{L}. \qquad (5)$$

The situation for stresses also changes: it is now impossible to speak of tangential shear stress acting on an infinitely thin surface: one block as a whole is displaced with respect to another, and force P producing this shear is applied to the upper block's center of inertia. The equation

$$\sigma_{xy} = P/L^2 \qquad (6)$$

is thus correct.

With Eqs. (5) and (6), Eq. (3) takes the form

$$\frac{1}{\eta} = \frac{L}{P}\left(v_x - v'_x\right). \qquad (7)$$

Parameter $1/\eta$, inverse to viscosity and referred to as fluidity, is introduced in Eq. (7).

As is well known, mobility q_j of the jth molecule is determined as

$$w_j = q_j p_j, \qquad (8)$$

where w_j is the velocity of a molecule, and p_j is the force acting on the molecule.

It is clear that we are speaking here of a force that is external with respect to the block, i.e., a force acting from the other block. The forces of interaction between the molecules of this block in our model have no effect on viscosity.

Force p_j can be estimated as

$$p_j = \frac{P}{L^2}\delta_j^2, \qquad (9)$$

where δ_j is the size of the jth molecule.

As can be seen from Eq. (8), parameter q_J acts as a coefficient of resistance to the motion of a molecule with respect to the medium. Velocity w_j should thus be considered as a relative velocity. As mentioned above, viscosity is governed by the Brownian motion of molecules. It is this motion that creates the resistance to the shear of one block with respect to another. Velocity w_j is therefore that of the jth molecule of the first block with respect to the other block. This allows us to write

$$v_x - v'_x = \frac{1}{N}\sum_{j=1}^{N} w_j, \qquad (10)$$

where N is the number of molecules in a block.

With Eqs. (8)–(10), Eq. (7) takes the form

$$\frac{1}{\eta} = \frac{1}{LN}\sum_{j=1}^{N} q_j \delta_j^2. \qquad (11)$$

Denoting the number of solvent and solute molecules in a block as N_w and N_g, respectively, we write

$$N = N_w + N_g. \qquad (12)$$

Denoting the mobilities of solvent and solute molecules as q_w and q_g, and the sizes of these molecules as δ_w and δ_g, respectively, we rewrite Eq. (11) as

$$\frac{1}{\eta} = \frac{1}{LN}\left(N_w q_w \delta_w^2 + N_g q_g \delta_g^2\right). \qquad (13)$$

Introducing the concentration of a dissolved compound via the relation

$$c = N_g/N \qquad (14)$$

and substituting this relation into Eq. (13), we obtain

$$\frac{1}{\eta} = \frac{1}{L}\left\{q_w \delta_w^2 - c\left(q_w \delta_w^2 - q_g \delta_g^2\right)\right\}. \qquad (15)$$

As before, denoting the parameters corresponding to a solvent and a solute with subscripts w and g and using Eq. (2), we write

$$q_w = \frac{h_w^2}{2\tau_w k_B T}\exp\left(-\frac{U_w}{k_B T}\right), \qquad (16)$$

$$q_g = \frac{h_g^2}{2\tau_g k_B T} \exp\left(-\frac{U_g}{k_B T}\right) \qquad (17)$$

for the mobilities of solvent and solute molecules.

Substituting Eqs. (16) and (17) into Eq. (15), we obtain

$$\frac{1}{\eta} = \frac{1}{2k_B T L}\left\{\frac{h_w^2\delta_w^2}{\tau_w}\exp\left(-\frac{U_w}{k_B T}\right)\right.$$
$$\left. - c\left[\frac{h_w^2\delta_w^2}{\tau_w}\exp\left(-\frac{U_w}{k_B T}\right) - \frac{h_g^2\delta_g^2}{\tau_g}\exp\left(-\frac{U_g}{k_B T}\right)\right]\right\}. \qquad (18)$$

Equation (18) is the sought theoretical concentration and temperature dependence of solution fluidity.

As can be seen from the above theoretical calculations, Eq. (18) was derived by assuming that the mobilities of both solvent and solute molecules are independent of the solution concentration (see Eqs. (16) and (17)). In other words, we assume that the introduction of a solute does not have any effect on the mobility of solvent molecules.

Generally speaking, this assumption may be doubted. At first glance, there are sufficient grounds for such doubts.

The environment of solvent molecules does indeed change after solute molecules are introduced into the system. It would seem that the presence of solute molecules in this environment must alter the activation energy of elementary displacement, and thus the mobility of solvent molecules.

The same reasoning can be applied to the mobility of solute molecules. It would seem any change in solution concentration that alters the environment of solute molecules must correspondingly change the activation energy, and thus the mobility of these molecules.

However, we do have the opportunity to validate the above assumption using experimental data. More specifically, if the assumption is valid, the fluidity must fall linearly as the concentration rises, as follows from Eq. (18). We intend to experimentally confirm this presumed property of fluidity up to solute concentrations so high that their order of magnitude is the same as that of the solvent concentration.

It is obvious that if our assumption is incorrect and solute molecules nevertheless alter the Brownian motion of solvent molecules, this will be more apparent when solute molecules considerably surpass solvent molecules in size. This was also one reason why we selected aqueous glucose solutions as our object of study.

EXPERIMENTAL

The concentration and temperature dependences that we experimentally established for the viscosities of the above solutions are plotted in Fig. 1. Measure-
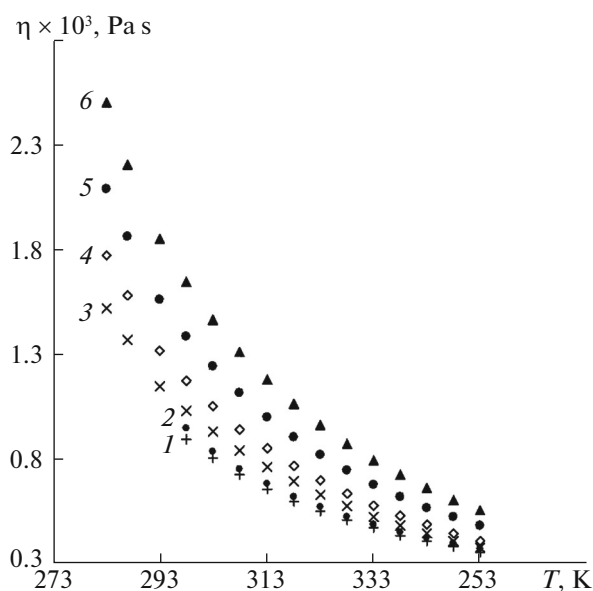

Fig. 1. Temperature dependence of the viscosity of aqueous glucose solutions at different concentrations: (*1*) 0.10, (*2*) 0.31, (*3*) 0.52, (*4*) 1.10, (*5*) 1.73, and (*6*) 2.44%.

ments were made using a capillary viscosimeter following the procedure in [5].

The fluidity–concentration dependences plotted using the data of Fig. 1 at different temperatures are shown in Fig. 2.

As can be seen from Fig. 2, the dependences of η^{-1} (s) in the temperature range of $T < 435$ K are linear for all of the studied concentrations. These dependences are also linear in the temperature range of $T > 435$ K, but only for concentrations higher than critical value c_1 of several percent in magnitude. By definition, $c_1 = 0$ in the region of $T < 435$ K. Dependence $c_1(T)$ is plotted in Fig. 2 as a dashed line.

Since dependences η^{-1} (*c*) for different temperatures are linear at $c > c_1$, we may state our assumption that molecule mobilities do not depend on concentration is true.

The experimentally confirmed linear dependence of fluidity on concentration allows us to use Eq. (18) to calculate activation energies U_w and U_g from the experimental data shown in Fig. 1. Applying the least-squares method, we obtained $U_w = 3.0 \times 10^{-20}$ J and $U_g = 2.8 \times 10^{-20}$ J.

RESULTS AND DISCUSSION

What is the molecular mechanism that produces the linear concentration dependence we found for fluidity?

As is well known [6], the hydrogen bonds that link water molecules form networks. The nodes of such a network are molecules that form three out of four
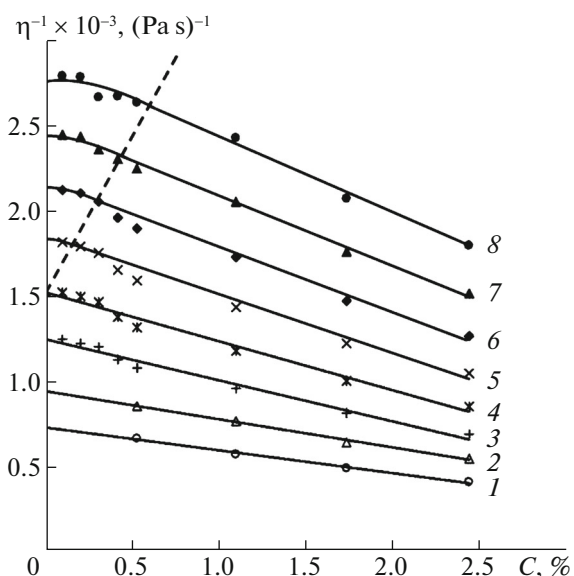
$\eta^{-1} \times 10^{-3}$, (Pa s)$^{-1}$

Fig. 2. Concentration and temperature dependence of the fluidity η^{-1} for aqueous glucose solutions at (*1*) 10, (*2*) 20, (*3*) 30, (*4*) 40, (*5*) 50, (*6*) 60, (*7*) 70, and (*8*) 80°C.

bonds with their neighbors. Network nodes are linked via chains built of molecules that have two bonds with their neighbors.

Using the obtained experimental data, let us estimate the direction of displacement that corresponds to an elementary act of Brownian motion. As a rough estimate, we shall consider a displacement that is transverse or longitudinal with respect to the orientation of a chain.

Moving in the transverse direction, a molecule must disrupt the two hydrogen bonds that link it with its neighbors in a chain. Since the energy of hydrogen bond disruption is 3.0×10^{-20} J [6], this means that the activation energy must be 6.0×10^{-20} J, which does not agree with the experimental value we obtained. Hence, an elementary displacement must be oriented along a chain.

However, we cannot speak about the displacement of an entire molecule along a chain, since such displacement is hindered by neighboring molecules. We can only speak of the displacement of some excitation along a chain. Such excitations are known in the theory of chain structure under the name of strain solitons (see, e.g., [7]). Elementary displacement h_w is in this case equal to the distance between the hindrances overcome by a soliton due to thermal fluctuations. Network nodes act as such hindrances. Parameter τ_w acquires the meaning of the time in which a soliton travels distance h_w, resulting in the estimate $\tau_w \approx h_w/c_w$, where c_w is the soliton velocity.

The molecules of neighboring chains interact weakly with one another. Neighboring chains there-

fore have virtually no effect on the motion of a soliton in a given chain.

For glucose molecules, it is more energetically advantageous to reside in interchain areas. Since the capabilities of water in the formation of hydrogen bonds are immediately exhausted, glucose molecules form hydrogen bonds between one another. A glucose network of hydrogen bonds thus appears in a solution.

However, if activation energy $U_w = 3.0 \times 10^{-20}$ J is very low for an elementary act of the Brownian motion of water molecules to be identified with water molecule displacement disrupting a chain of hydrogen bonds, there is no reason to think that an entire glucose molecule, which considerably surpasses a water molecule in size, is displaced during an elementary act of Brownian motion. The corresponding activation energy is much too low to accomplish this ($U_g = 2.8 \times 10^{-20}$ J). It only remains to say that the mobility in the chains of the glucose network is also due to the motion of solitons.

Hence, the solution contains are two hydrogen bond networks that weakly interact with each other. In each network, its own solitons can perform Brownian motion. The weak interaction between the networks means the contributions to the flow of a solution from the two types of solitons is virtually independent, allowing us to explain the independence of the mobilities of water and glucose molecules from the concentration.

Since the particles that perform Brownian motion are solitons, parameter c becomes the concentration of solitons. As mentioned above, experiments show that at a concentration of glucose that exceeds a certain critical value, the fluidity of a solution falls linearly as the amount of glucose rises. The proposed mechanism thus agrees with the experimental data if the number of solitons responsible for the displacement of glucose molecules in a solution and the number of solitons responsible for the displacement of water molecules are proportional to the amounts of glucose and water in a system, respectively. In our opinion, this can be considered natural, at least in the first approximation.

The observed deviation from linearity in the concentration dependence of fluidity at $T > 435$ K in the region $c < c_1$ can also be explained using the proposed mechanism. As was shown in [8], the structure of water is considerably transformed in the above temperature region, and this is apparent in the deformation and rupturing of hydrogen bonds. The latter leads to destruction of the network, and the total number of solitons falls at temperatures $T > 435$ K. However, the model that is considered in this work and predicts a linear fluidity–concentration dependence is based on the assumption that the number of particles performing Brownian motion (in this case, solitons) remains unchanged. In our opinion, this is the reason for the deviation from linearity in the fluidity–concentration dependence. Since linearity is restored at higher con-

centrations, we may conclude that the presence of glucose molecules in the system stops the temperature-induced disruption of hydrogen bonds between water molecules.

CONCLUSIONS

The structure of an aqueous glucose solution can thus be presented as a combination of two weakly interacting networks. The first network is formed by the hydrogen bonds that link water molecules to one another, while the second is formed by the hydrogen bonds that link glucose molecules to one another.

The viscosity (and thus the fluidity) of a solution in such a network structure is due to the Brownian motion of solitons along the chains constituting both networks. The displacement of a soliton during an elementary act of Brownian motion is equal to the distance between network nodes. A node acts as a hindrance that is overcome by a soliton due to fluctuations.

The weak interaction between the networks means that the contributions to the fluidity of a solution from the motions of solitons in both networks are virtually independent.

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