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Peculiarities of the light scattering in dilute water-glucose solutions

This work is devoted to the behavior of the light scattering coefficient study in dilute water-glucose solutions near the characteristic temperature $T=315\text{K}$ (42^0C). Two methods of the integral light scattering are applied. Evolution and temperature dependence of the angular anisotropy index for different solutions' concentrations are studied. We detected peaks of the light scattering intensity in a 5 wt % aqueous solution of glucose near the characteristic temperatures of a human body. In our opinion, this could be related to the percolation cluster formation and solution's structuring.

Introduction. Glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is a carbohydrate of the great biological importance. It is highly soluble in water, where exists in the two anomeric α and β forms [1], characterized by a similar cyclic structure. Glucose is a simple sugar that constitutes the basic units of important polysaccharides, such as trehalose and dextrans; thus it represents a suitable system for the characterization of the structure and the dynamics of aqueous sugar solutions [2]. Carbohydrates have a good potential in cryopreservation and cryoprotection. They have already been used as antifreezes [3-5].

There are many modern studies of the dynamical processes in dilute aqueous solutions of biological substances and alcohols. Kaminski *et al.* [6] analyses dielectric and FTIR measurement on D-glucose in its supercooled liquid phase. There are two relaxation modes and the slower one characterizes the cluster relaxation process. FTIR measurements of the OH bands allow authors to conclude that at temperatures above 366K the clusters become unstable and likely disintegrate.

In [7-8] authors studied aqueous solution of glucose using dynamic light scattering (DLS). Data show the existence of clusters in a size range between 30 and 60 nm and a percolation of a hydrogen-bonded (H-bonded) glucose network.

The characteristic temperature of water, where H-bonded network in molecular interaction tends to zero, is close to $T=315\text{K}$ [9-11]. At higher temperatures the character of the molecular motion becomes similar to the argon-bonded substances.

For albumin, a human blood protein, parameters of it's molecules are critically changed near $T=315\text{K}$ [12].

The similar percolations were detected in some dilute aqueous solutions in the anomalous light scattering studies [13-14]. It was shown that the size of inhomogeneities obtained by a correlation spectroscopy ten times differs with that obtained by an angular anisotropic scattered light. A time factor is also significant. Optical and dielectrical characteristics of aqueous solutions reaches their equilibrium values in a long time - from several days to several weeks [15].

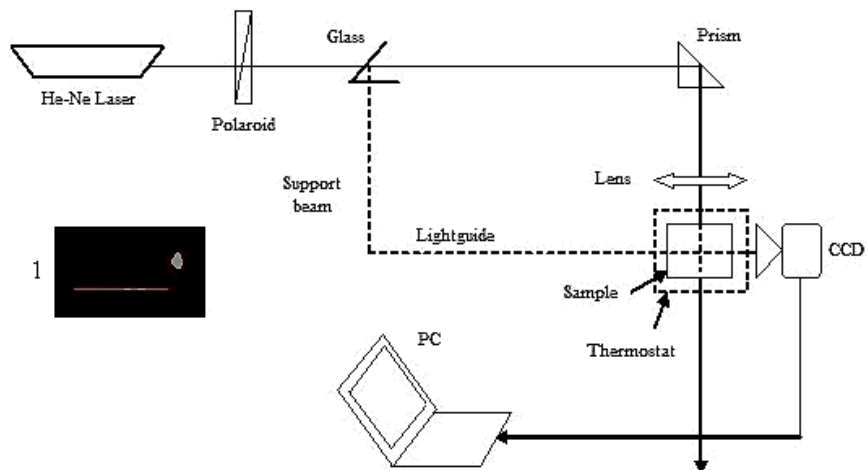


Fig. 1 Schematic diagram of the integral light scattering instrument; 1 – a photo of the scattered light (a line) and the reference beam (a point) obtained by CCD.

The main aim of this article is to present the light scattering study of the temperature, concentration and time dependences of dilute water-glucose solutions' parameters near the characteristic temperatures.

Experiment. Aqueous solutions of glucose of the 1, 5, 9 and 17 wt % glucose concentrations were produced by mixing a highly pure glucose powder with double distilled water until completely dissolved. Dilute water-glucose solutions were studied by two integral light scattering methods. In the first one measurements of the light scattering intensity were conducted by classical methods [16-18], but with an upgraded implementation of a reference beam derived from Fresnel reflection. The reference beam was needed to eliminate the influence of the laser intensity's instability and CCD sensitivity to the measurement results in long-term monitoring.

In Fig. 1 a linearly polarized light from He-Ne Laser LHN-215 with a wavelength $\lambda=633\text{nm}$ and a vertical orientation of the polarization vector passes through a Polaroid and then is divided in two with a Glass plate. The intensity of the primary beam almost unchanged and the reflected beam is formed. According to Fresnel law [19] the intensity of the reflected beam can be changed from 0 to 100% of the primary beam intensity. Therefore, we can manage the reference beam intensity with little energy loss of the primary beam, which is important for small scattering coefficients. Reflected light is passed through the light guide and intersected the primary beam in the sample at the angle 90° to the reference beam. The intensity of the reference beam was chosen approximately equal to the primary beam intensity. The scattered light and the reference beam are registered by a CCD-matrix and recorded to a PC hard drive.

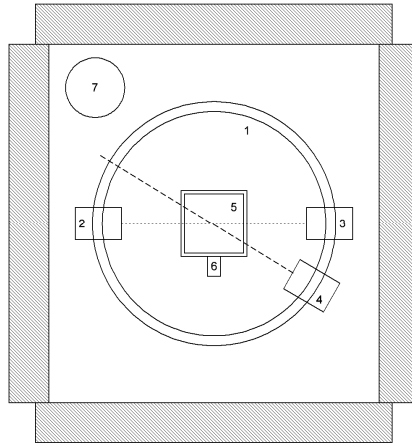


Fig.2 Schematic diagram of the optical instrument: 1 – steel disc; 2, 3 – photo-sensors OPT101; 4 – a semiconductor laser diode; 5 – sample; 6 – a semiconductor digital temperature sensor DS18B20; 7 – electric heater.

Thermostat is placed on the table of a goniometer Г-1,5. This allowed us to control the angle scattering with an accuracy up to 20". Optical vibrations are absorbed by the optical table.

Fig. 1.1 represents the photo of the scattered light (a line) and the reference beam (a point) obtained by CCD. The original program “Intensity” is used for the calculations of the average light scattering intensity.

We used the theory of Debye [20] for calculations. The angle anisotropy index is $Z = I_{45^\circ} / I_{135^\circ}$, here, I_{45° and I_{135° – intensities corresponded to angles 45° and 135°. Z parameter allows us to calculate a size of inhomogeneities in accordance with a relation (1) depending on the light scattering intensity, on the scattering angle and the quantity $\Delta T = T - T_{critical}$ (the difference between the measurements temperature and the critical temperature of stratification).

$$I_\Theta = C \frac{\frac{\Delta T}{T_K}}{\frac{\Delta T}{T_K} + \frac{8\pi^2 l^2}{3\lambda^2} \sin^2 \frac{\Theta}{2}} (1 + \cos^2 \Theta), \quad (1)$$

where C – a constant at the point T, Θ – the angle between the laser beam direction and the observation point, λ – wave length of the emitted light, l – the radius of molecular interactions.

The second method of the light scattering intensity study is realized by an original optical experimental instrument shown in Fig. 2. The angular anisotropy of the scattered light was measured.

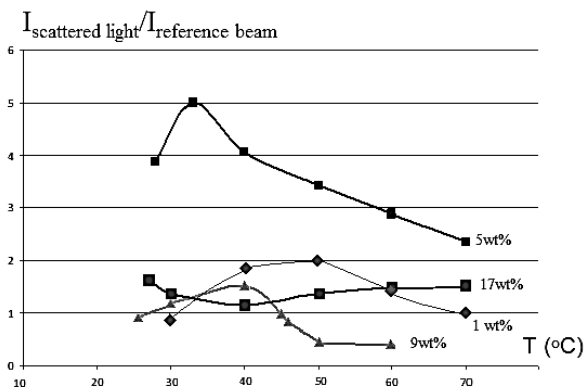


Fig.3 Temperature dependences of the light scattering intensity in dilute water-glucose solutions of different concentrations.

Two photosensors OPT101 2 and 3 with a semiconductor laser diode 4 are attached on a steel disk 1. In the center of the disk 1 is placed a sample of the studied solution 5. All these pieces are put into a metallic light-tight box. The box is insulated by penopoliestirol and equipped with a semiconductor digital temperature sensor DS18B20, 6, and the electric heater 7. A car battery with a capacity of 60 A/h is used as a power supply. It's power is enough for the instrument's work for 30 days with a turned on thermostat. The system is controlled by the board STM32-Discovery with the microcontroller STM32F100R8T6B. The microcontroller has ADC with 16 channels and 12 bits, 51 lines IO, 64kB program's memory (FLASH) and 4kB RAM.

The board STM32-Discovery is installed on a breadboard where are also installed a power supply, a heater control and a laser diode control keys, ICs of a matching between the microcontroller ADC inputs to the photosensors OPT101 outputs, a connector for the temperature sensor and connector for memory card SD.

Results and discussion. In Fig. 3 temperature dependences of the light scattering in water-glucose solutions are shown. The peak of the light scattering is observed at the concentration 5 wt% near $T=35^{\circ}\text{C}$ and at the water characteristic temperature.

To explain this phenomenon it is appropriate to draw an analogy with aqueous solutions of glycerol and albumin studies [21, 12]. It was found that the maximal value of the scattering coefficient for dilute water-glycerol solutions is observed for a solution of $x=0,046$ mole fraction of glycerol, which corresponds to the formation of the percolation cluster in the solution. For solutions with other mole fraction values the light scattering peak's value decreases and it's position is shifted to higher temperatures.

An additional low-concentration peak of the light scattering in water-glycerol solutions is associated with a structuring of solutions and a peculiar cluster formation [21]. Critical behavior of water-albumin solutions is explained by a phase transition – pre-denaturation [12]. All these facts allow us to assume that the peculation in water-glucose solutions can be explained in terms of a solutions' structuring.

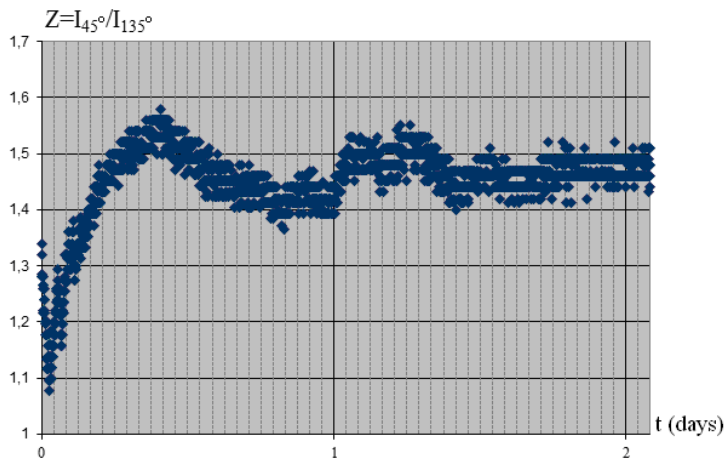


Fig.4 Time dependence of the angular anisotropy index $Z = I_{45^\circ} / I_{135^\circ}$ in 5 wt% water-glucose solution at room temperature.

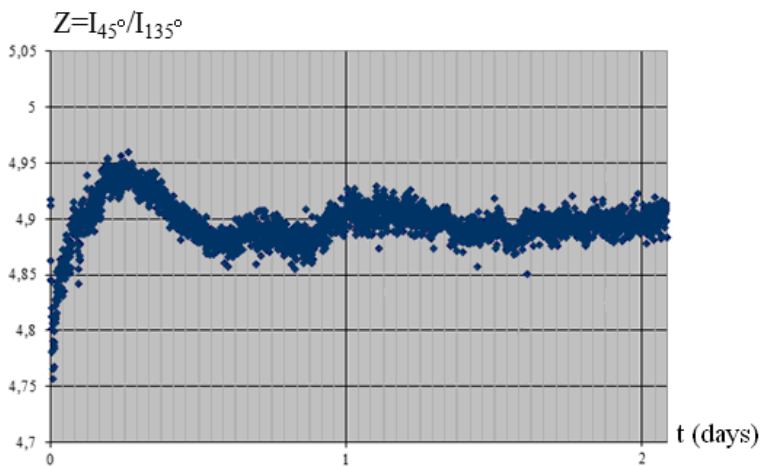


Fig.5 Time dependence of the angular anisotropy index $Z = I_{45^\circ} / I_{135^\circ}$ in 5 wt% water-glucose solution at 28°C.

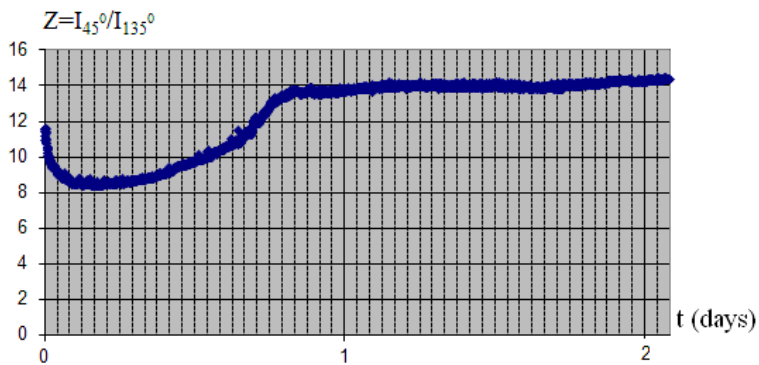


Fig.6 Time dependence of the angular anisotropy index $Z = I_{45^0} / I_{135^0}$ in 9 wt% water-glucose solution at room temperature.

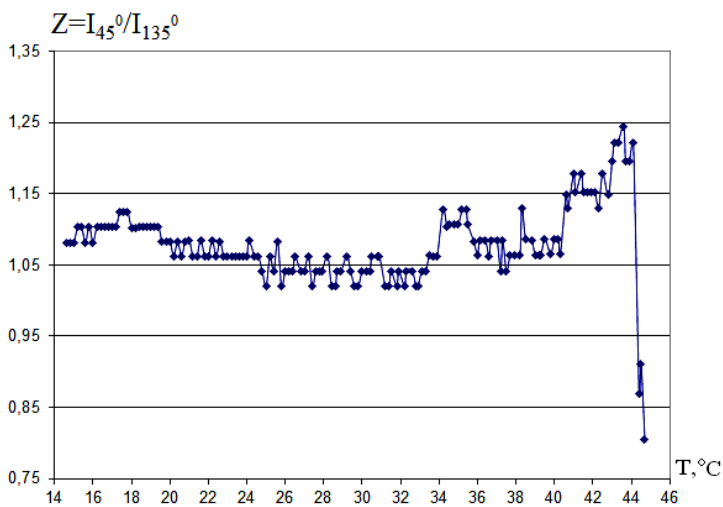


Fig.7 Temperature dependence of the angular anisotropy index $Z = I_{45^0} / I_{135^0}$ in 5 wt% water-glucose solution.

We studied relaxation processes in water-glucose solutions by an instrument in Fig. 2. Results of the evolution of the angular anisotropy index for 5 wt% and 9 wt% glucose concentrations are presented in Fig. 4, 5 and 6.

Obviously, the angular anisotropy index changes non-monotonically and reaches its equilibrium value in a few days. In this case, the initial stages of the 5 wt% and 10wt% dependences are radically different.

It is important to note that the evolution of water-glucose solutions' parameters significantly differs from those of water-alcohol solutions. The angular anisotropy index changes not more than in 10% range. Therefore, in homogeneities grow slightly, but we can see evolution of the angular anisotropy depending on the sample's temperature. Measurements are conducted at room temperature.

It is established that the evolution of solutions occurs, the equilibration time is about a week, the temperature dependence of the angular anisotropy index is significant.

We also conducted the measurements of the angular anisotropy index depending on the sample's temperature. Results are presented in Fig 7. This dependence has two peculiarities at characteristic temperatures 36°C and 42-44°C.

Conclusions.

1. The light scattering intensity in water-glucose solutions increases sharply at the temperature of 35°C, has a maximum at a concentration of 5 wt% that is similar aqueous solutions of alcohols, which suggests that the characteristic temperatures are associated with structural peculiarities of water.

2. The angular anisotropy of light scattering in water-glucose solution indicates the existence of ~100nm mesoscale inhomogeneities in solutions and a slow equilibrium achieving (about a week), which strongly depends on the temperature.

References:

1. *Sugget A., Franks F. (Ed.) Water a comprehensive treatise, aqueous solutions of amphiphiles and macromolecules // Plenum Press, New York, 1975. – Vol. 4.*
2. *Fioretto D., Comez L., Gallina M.E., Morresi A., Palmieri L., Paolantoni M., Sassi P., Scarponi F. // Chemical Physics Letters. – 2007. – V. 441. – P. 232–236.*
3. *Amalfa F. // Biophysical Journal. – 2000. – V. 78. – P. 2452.*
4. *Benaroudj N., Hee Lee D., Goldberg A.L. // Journal of Biological Chemistry. – 2001. – V. 276. – P. 24261.*
5. *Crowe J.H. // Annual Review of Physiology. – 1998. – V.60. – P. 73.*
6. *Kaminski K., Kaminska E., Adrjanowicz K., Wojnarowska Z., Włodarczyk P., Grzybowska K., Dulski M., Wrzalik R. and Paluch M. // Physical Chemistry Chemical Physics. – 2010. – V.12. – P. 723–730.*
7. *Sidebottom D.L. // Physical Review E. – 2007. – V. 76. – P. 011505.*
8. *Sidebottom D.L. and Tri D. Tran // Physical Review E. – 2010. V. 82. – P.051904.*
9. *Bulavin L.A., Fisenko A.I., Malomuzh N.P. // Chemical Physics Letters. – 2008. – V. 453, P. 183.*

10. Bulavin L.A., Malomuzh N.P., Pankratov K.N. // Journal of Cell Science. – 2006. – V. 47. – P. 52.
11. Lokotosh T.V., Malomuzh N.P., Zakharchenko V.L. // Journal of Cell Science. – 2003. – V. 44. – P. 1101.
12. Bardik V., Gotsulskii V., Pavlov E., Malomuzh N., Nerukh D., Yanchuk I., Lavoryk S. // Journal of Molecular Liquids. – 2012. – V. 176. P. 60-64.
13. Chechko V.E., Gotsulsky V.Ya., Malomuzh M.P. // Condensed Matter Physics. – P. 2013. – V. 16. № 2. DOI: 10.5488/CMP.16.23006.
14. Gotsulskiy V.Ya., Malomuzh N.P., Chechko V.E. // Journal of Physical Chemistry. – 2013. – V. 87, № 10. – P. 1660–1667.
15. Bulavin L.A., Gotsulskiy V.Ya., Chechko V.E. // Ukrainian Journal of Physics. – 2014. – V. 59. – P. 689.
16. Chechko V.E., Gotsulskiy V.Ya., Zaremba V.G. // Journal of Molecular Liquids. – 2003. – V. 105, № 2-3. – P. 211.
17. Chechko V.E., Zaremba V.G. // Chemical physics. – 1993. – V. 12, № 7. – P. 1036-1039.
18. Cummins H.Z., Pike E.R. Photon Correlation and Light Beating Spectroscopy. – Plenum Press, New York, 1974. – P. 285.
19. Landsberg G.S. Optics. – Fizmatlit, Moscow, 2006.
20. Debye J.P. The collected papers of Peter J. W. Debye. – Interscience, New York-London, 1954.
21. Chechko V.E. Light scattering study of aqueous solutions of glycerol [in Russian] // Ukrainian Journal of Physics. – 2001. – V. 46, № 9. – P. 920-921.

Ханчич К.Ю., Мельник Ю.А., Гоцульський В.Я.
Особливості розсіяння світла в водних розчинах глюкози

У даній роботі досліджено поведінку коефіцієнта розсіяння у низько концентраційних водних розчинах глюкози поблизу характеристичної температури 315K (42°C). Методами інтегрального розсіяння світла отримано температурні залежності інтенсивності світлорозсіяння для розчинів різних концентрацій. Виявлено існування максимуму світлорозсіяння при температурі, близькій до нормальної температури людського тіла, та масовій концентрації розчину 5%. Є всі підстави вважати, що це пояснюється утворенням кластерів та структуриванням розчину.

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Особенности рассеивания света в водных растворах глюкозы

В данной работе исследовано поведение коэффициента светорассеяния в низкоконцентрационных водных растворах глюкозы вблизи характеристической температуры 315K (42°C). Методами интегрального светорассеяния получены температурные зависимости интенсивности рассеянного света для растворов различных концентраций. Обнаружено существование максимума светорассеяния при температуре, близкой к нормальной температуре человеческого тела, и массовой концентрации 5%. Есть все основания полагать, что это объясняется образованием кластеров и структурированием раствора.