Influence of hydrogen bonding on the elastic properties of molecular glassforming liquids under high pressure

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Abstract. We present ultrasonic study of bulk modulus of liquid glycerol and propylene carbonate (PC) at room temperature under high pressure up to 0.6 and 1 GPa, respectively. Pressure dependence of the isothermal bulk modulus, recalculated from the ultrasonic adiabatic data, is almost linear for the both liquids with relatively similar slopes, in spite of the initial value of bulk modulus being twice higher for glycerol due to the presence of the hydrogen bonds. The values of pressure derivative (7.8 for glycerol and 8.6 for PC) indicate that the intermolecular interaction in the both liquids is close to the Lennard-Jones potential.

1. Introduction

Intermolecular interaction in molecular liquids with uncharged molecules is caused by the van der Waals forces. However, in many cases, hydrogen bonds, being a complex ion-covalent interaction between the strongly electronegative atoms by means of hydrogen, can produce a significant contribution to the interaction. The energy of the hydrogen bonds is much lower than energies of ion and covalent interactions, but higher than typical energy of the van der Waals intermolecular forces, that can significantly influence on thermodynamic properties of substances, e.g., on the high boiling point of water. From structural point of view, hydrogen bonds may affect orientational correlations of neighbor molecules in liquid and an orientational short range order of molecules in the glass. The different intermolecular potentials (with and without contribution of the hydrogen bonds) should also be directly observed as an expected difference of elastic properties.

Effect of hydrogen bonding on the intermolecular interactions can be illustrated by an example of glycerol C$_3$H$_8$O$_3$ and propylene carbonate (PC) C$_4$H$_6$O$_3$. Both substances have quite similar size and mass of molecules, densities and temperature dependence of density $\rho(T)$, as well as glass transition temperatures (157 K for PC and 187 K for glycerol) [1,2]. At the same time, each molecule of glycerol has three hydroxyl OH groups, which can be involved into hydrogen bonding, while 3 oxygen atoms in the PC molecule are connected only with carbon in the molecular skeleton and cannot virtually contribute to hydrogen bonds. As a result of this, the velocity of longitudinal ultrasonic waves in liquid glycerol is by a factor >1.5 higher than that in PC [3-5]. Correspondingly, bulk modulus of liquid glycerol is by two times higher than that of PC.

Whereas the difference in elasticity of liquid glycerol and PC is remarkable at normal conditions, it is not clear how this difference should change with pressure. Pressure dependence of bulk modulus is direct test of change of intermolecular potential parameters. In this respect, ultrasonic technique is...
very adequate method for accurate measurement of elastic characteristics (bulk modulus $B$ for liquids), including pressure derivative of $B$ and its nonlinearity with pressure (see examples for solid molecular systems under pressure in [6-8]).

Here, we present ultrasonic study of bulk modulus of liquid PC and glycerol under high pressure up to 0.6 and 1 GPa, respectively.

2. Experimental setup
Experiments were carried out using a high-pressure ultrasonic piezometer based on piston-cylinder device [9]. During the experiment simultaneous measurements of sample length and transit time of ultrasonic wave were made in pressure range up to $\approx 1$ GPa (here, the maximum pressure is defined by mechanical stability of capsule with liquid) at room temperature 295 K, allowing to calculate density, ultrasonic velocity and bulk modulus of a sample. Liquid glycerol and PC were placed in a teflon capsule (with internal diameter of 16 mm and height of 8 mm) with copper caps (with thickness of $\approx$1 mm). Glycerol was purchased from Aldrich chemical company and PC from Acros Organics. The purity of both materials was guaranteed to be higher than 99.5%. The estimated pressure uncertainty was $\pm 0.05$ GPa. The measurements of the transit time (with uncertainty within 0.001 $\mu$s) of longitudinal ultrasonic pulses were performed by the pulsed ultrasonic method using LiNbO3 plates as piezoelectric sensors with carrier frequency 10 MHz. The transit time of ultrasonic pulses was directly measured by the system on the basis of the National Instruments PXI platform. Changes in the ultrasonic signal paths were also measured with uncertainty within 5 $\mu$m using dial-type micrometer indicators. The density of samples under pressure was determined from the change in their length. Bulk modulus was calculated from the ultrasonic data using the approximation of homogeneous isotropic medium.

3. Experimental results and discussion
Ultrasonic measurements at megahertz frequencies provide experimental data for adiabatic elastic properties. The relationship between the isothermal bulk modulus $B_T$ and adiabatic modulus $B_S$ is determined by equation

$$\frac{B_S}{B_T} = 1 + \frac{\alpha^2 T B_S}{\rho c_P} = 1 + \alpha T,$$

(1)

where $\alpha$ is the coefficient of volume thermal expansion, $c_P$ is the specific heat capacity at constant pressure, $\rho$ is the density of a substance, and $\gamma$ is the Gruneisen parameter close to unity for condensed state. The difference between $B_T$ and $B_S$ at room temperature is equal to $\approx 22\%$ for PC and to $\approx 14\%$ for glycerol, and is relatively large due to the large values of volume thermal expansion coefficients [10] (for glassy states of these substances as well as for majority of solids the difference between $B_T$ and $B_S$ is of the order of 1-3%). Figure 1 presents the pressure dependence of the isothermal bulk modulus $B_T$ at room temperature for both studied liquids. Both were recalculated from directly obtained ultrasonic data for adiabatic bulk moduli under pressure, taking into account the data of [10] on the volume thermal expansion of glycerol and PC under pressure and the value of Gruneisen parameter $\gamma$ $\approx 1$, that was checked at room pressure. The maximum pressure ($0.6$ GPa) achieved during the measurement of glycerol (figure 1) was restricted by strong absorption of ultrasonic wave in the sample due to approach to the glass transition region. In PC, there is no glass transition in this region and pressure range (up to 1 GPa) is limited only by possibilities of the experimental setup and stability of capsule.

First, although the initial value of $B_T$ is twice higher for glycerol (figure 1), pressure dependence of bulk modulus is quite similar for both substances, and both bulk moduli grow linearly at the relatively similar rate under pressure, $(\partial B_T / \partial P)_T \approx 7.8 \pm 0.2$ for glycerol and $(\partial B_T / \partial P)_T \approx 8.6 \pm 0.2$ for PC. The other important fact is that both pressure derivatives of bulk modulus $B'(P)$ are close to 8. It is known that for central interparticle n-m potential $U = A/V^n - B/V^m$, pressure derivative of bulk
modulus is $B'(P) = m + n + 2$ [11]. For Lennard-Jones potential, $n=4$, $m=2$, and, so, $B'(P) = 8$. This means that the interaction in liquid glycerol and PC can be approximately described by the Lennard-Jones potential, at least in the considered pressure range, and hydrogen bonds in glycerol, diminishing compressibility with respect to that in PC, do not significantly influence on the character of volume dependence of the van der Waals intermolecular forces. The small difference between the derivatives of bulk moduli for the both liquids results in the fact that the elastic moduli values approach each other with increasing pressure.

**Figure 1.** Pressure dependence of the isothermal bulk modulus $B_T$ at room temperature 295 K

The measurements of the relationship between pressure and volume using a high-pressure ultrasonic piezometer are not quite accurate, despite the corrections with regard to the friction, hysteresis, and deformation of the components of the piston-cylinder device [9]. A more accurate equation of state $V(P)$ can be obtained by the pressure integration of isothermal compressibility (the inverse bulk modulus).

**Figure 2.** Relative volume change under pressure at room temperature 295 K
Pressure dependence of relative volume $V/V_0$ is presented in figure 2 for both substances. They show the typical behaviour for liquids at elevated pressures. At 0.6 GPa, volume of glycerol decreases by $\approx 9.5\%$ and volume of PC - by $\approx 13\%$. We compared our data with equation of state for glycerol and PC given by Reiser et al. [10] from direct volumetric measurements. While our results on propylene carbonate are in a perfect coincidence with data from [10], in the case of glycerol we observe some differences. Compressibility of glycerol defined from the ultrasonic study is slightly less than that from the volumetric measurements.

Thus, using glycerol and propylene carbonate as model molecular liquids with and without hydrogen bonds, we have shown that, whereas hydrogen bonds make intermolecular interaction stronger, they do not significantly influence on pressure derivatives of bulk modulus under pressure. This implies that glycerol and PC have quite similar functional forms of potential with respect to change of volume and intermolecular distances.

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