Ultrasonic study of 1-propanol glasses with various thermobaric histories during the glass–liquid transition

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Abstract. Ultrasonic method has been used for experimental investigation of primary alcohol 1-propanol, which can be easily glassified at low temperatures. Two types of glasses with different thermobaric histories were obtained by different paths on the $T$–$P$ diagram and were comparatively studied at isobaric heating during glass–liquid transition. At low temperatures, the elastic properties of glasses are different by tens of percent, but with increasing temperature the difference decreased and totally disappeared in the liquid phase.

1. Introduction

Simple liquids are ergodic systems where metastable state can exist for only very short times. Glasses, unlike liquids, are non-ergodic systems, and their properties depend not only on external macroparameters, such as temperature and pressure, but also on the way of their fabricating on the $T$–$P$ diagram [1]. A different pressure history affects glass rigidity [2] and the glass transition temperature $T_g$ [3]. The cooling rate of the liquid to produce glass affects the short-range order and density [4,5]. Previously we have studied the glasses of propylene carbonate with different thermobaric history [6, 7]. It turned out that the greatest differences were observed in shear elasticity and glass transition temperatures. To continue the investigation of the influence of thermobaric history on the properties of glasses we chose 1-propanol. This substance is a monohydric alcohol with the chemical formula C$_3$H$_7$OH. It contains one hydroxyl group OH, which can organize a hydrogen bond with two neighboring molecules. 1-propanol has high values of derivatives of ultrasound velocities with respect to pressure at room temperature [8] and high compressibility in the liquid state [9].

In this work, we have studied two types of 1-propanol glass with various thermobaric histories. The first one was obtained by cooling liquid propanol from room temperature (295 K) to the temperature of liquid nitrogen (77 K) at 0.1 GPa. The resulting glass is called LPG—low pressure glass. Another type, called high-pressure glass—HPG, was obtained by initial pressurising of liquid propanol up to 1 GPa at 295 K, quenching to 77 K and then decompressing to 0.1 GPa. The cooling rate for both glasses was about 15 K per minute.
2. Experimental
The studies were carried out using an ultrasonic piezometer created based on a high-pressure piston-cylinder device [10]. Temperatures were changed from 77 to 300 K. The temperature was measured using 4 copper-constantan thermocouples. The accuracy of the temperature determination was about 1 K. The length of the sample was determined by the two dial-type indicators with an accuracy of 5 µm. To generate and detect the ultrasonic signal we used piezoceramic plates of lithium niobate LiNbO₃ with carrier frequencies of 5 (for transverse) and 10 MHz (for longitudinal wave). The sample volume under pressure was initially determined from change of its length, and subsequently the equation of state of liquid sample above the glass transition was calculated by integration of compressibility (reverse bulk modulus) with an accuracy of several percent. In order to calculate the shear $G$ and bulk $B$ elastic moduli, we used the homogeneous isotropic medium approximation.

3. Results and discussion
We investigated the elastic properties of 1-propanol in the regime of natural heating from 77 to 300 K during the glass to liquid transition. The velocity of the longitudinal ultrasonic wave is more than 2 times higher in the glassy state than in the liquid (1.2 km/s at 295 K and 2.6 km/s at 77 K). The difference in the densities of the two types of glasses turned out to be small, the HPG is denser by 2% than the LPG at 77 K.

However, the bulk modulus $B$ (figure 1) and the shear modulus $G$ (figure 2) demonstrate significant differences. Thus, bulk modulus for HPG is 10% higher than that for LPG at 77 K.
With increasing temperature and softening of glass, this difference decreases, and the properties of liquids obtained from the heating of different glasses do not differ, which follows from the ergodicity of the liquid phase. The small discrepancy between the graphs in the liquid phase is within experimental errors. During heating at low pressures of 0.1 GPa, there is a clear kink on the bulk modulus graph, related to the glass transition temperature $T_g$. In the very viscous liquid state, above $T_g$, there are no experimental data on ultrasound velocities. This is due to the strong absorption of ultrasonic waves in the substance in this region. The difference between the shear moduli $G$ (see figure 2) for different glasses is more remarkable—25–30%. One can propose that such a significant increase in elastic moduli is associated with the closure of nanopores in the liquid at 1 GPa and a corresponding change in the intermediate range order structure of the HPG. Unfortunately, our experimental setup does not allow in the most liquids to carry out measurements above $T_g$ in the region of a supercooled liquid with a complex viscoelastic behavior due to the strong attenuation of ultrasonic waves in the substance. At higher temperatures in a nonviscous liquid state, the modulus $G$ vanishes at our experimental frequencies.Bulk modulus $B$ decreases from 4.5–5 (77 K, glass, pressure 0.1 GPa) to 1.5 GPa (295 K, liquid).

4. Conclusion
To summarize, the elastic properties of glassy 1-propanol depend strongly on the thermobaric history. Glass obtained at high pressure has a significantly higher bulk and shear moduli compared to glass obtained at low pressure. One can expect that characteristics of other glasses can be varied in some range by changing the conditions of their fabrication.
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