Ultrasonic Study and Dielectric Spectroscopy of Pyridine under High Pressures at different Temperatures

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Pyridine is of particular interest in terms of its rich polymorphism [1,2]. With an increase in pressure, pyridine crystallizes at room temperature into an disordered phase I, which, with a further increase in pressure, transfers into an ordered phase II. According to the literature, melting occurs at an ambient temperature of 0.55 GPa [2], but reports indicate 1 GPa as the onset of crystallization [3]. In addition it was reported that the glassy phase is formed at atmospheric pressure and low temperature.

We present the high pressure ultrasonic study and dielectric spectroscopy of liquid and solid pyridine. Both of the methods provide complementary pictures of the transitions in pyridine under pressure. We employ an original experimental facility based on the modified high-pressure piston-cylinder device to map the location of phase boundaries by making simultaneous measurements of density, bulk modulus, shear modulus and Poisson's ratio. The measurements were performed by the pulsed ultrasonic method using $LiNO_3$ plates as piezoelectric sensors with carrier frequencies of 5-10 MHz. Pyridine phase diagram was determined at 77-295 K in the pressure range $0 < P < 1.1$ GPa. The phase transitions were detected by jumps in experimental pressure dependencies of the lengths of samples and transit times of ultrasonic waves. The equation of state of liquid and solid pyridine was determined up to 1.1 GPa from ultrasonic measurements of bulk modulus and is in good accordance with the previous equations developed from volumetric data [1]. Crystallization of liquid pyridine is accompanied by a volume jump (~ 2.5%). During the phase transition I – II, no volume change was detected, but obvious anomalies in the velocity and amplitude of the longitudinal ultrasound were revealed. The strong dependence of pyridine's crystallization on the loading rate was revealed with increasing pressure in our experiments. We measured the bulk and shear moduli and Poisson's ratio of glassy pyridine up to 1.1 GPa (T=77K). High-pressure dielectric spectroscopy experiments were carried out in Toroid type anvils in the P-T region $P < 4.2$ GPa and $150\ K < T < 350$ K. During isobaric cooling in the range from 0 to 0.6 GPa, pyridine goes into a mixed crystalline + glassy state, as evidenced by the presence of a characteristic relaxation process. The glassy state is unstable, and upon subsequent heating crystallization occurs, accompanied by followed by a decrease in the amplitude of the relaxation process to zero and a transition from the orientationally ordered phase, characterized by low dielectric constant values, to the orientationally disordered phase. Many relaxation and elastic properties of pyridine can be qualitatively described using the soft sphere or the Lennard-Jones model. However, for a quantitative description of the entire set of experimental data these models is not enough. In addition, the value of the Poisson coefficient for glassy pyridine indicates a significant contribution of non-central forces to the intermolecular potential.

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