Hydrogen-bonded substances under high pressure: Ultrasonic study of the low temperature phase diagrams of methanol, ethanol and H$_2$O ice

E.L.Gromitskaya, O.V.Stal'gorova, O.F.Yagofarov, V.V.Brazhkin, A.G.Lyapin and S.V.Popova

Institute for High Pressure Physics, Russian Academy of Sciences

Troitsk, Moscow region, 142190, Russia,

Email:grom@hppi.troitsk.ru

The ultrasonic method is used to study the phase diagrams of methanol and ethanol in the range of temperatures 90-290 K and pressures 0-12 GPa. We obtained the pressure and temperature dependences of the longitudinal wave velocity, the modulus of elongation (for liquids, coincident with the bulk modulus) and the densities of crystalline and liquid methanol and ethanol phases. We observed weak anomalies in the dependences of the longitudinal wave velocity in the liquid methanol and an anomalous additional liquid densification, corresponding to these weak anomalies in the ranges of temperatures 230-250 K and pressures 0.2-0.6 GPa, which may be due to the structural changes in the liquid phase. Methanol demonstrates more complicated phase behavior under pressure in contrast to ethanol, phase diagram of which is quite simple in the studied pressure-temperature area. We associate the differences in the phase diagrams of methanol and ethanol to the stronger hydrogen bonds in methanol and to simpler structure of its molecules. This trend is directly illustrated by the data for H$_2$O water, which has one of the simplest molecule, the strong hydrogen bonding, and quite complicated phase diagram.

Introduction

Methanol and ethanol are sufficiently simple model objects that can be used to study the nature of intermolecular interactions in systems with hydrogen bonds. Unlike ice and water, which under normal conditions are substances with strong tetrahedrally-ordered hydrogen bonds, methanol and ethanol are regarded as “classical” objects with a moderate hydrogen interaction (most likely, weak for ethanol) and with a chain-like structure in both crystalline and liquid states [1-5]. Knowledge of the effect of pressure (p) and temperature (T) on the structure and physical properties of these objects is very useful for understanding the nature of these systems, which clarify the peculiarities in the behavior of hydrogen bonds under these conditions. Unlike water, alcohols are much less studied; experimental data on their p-T diagrams and physical properties is scanty and data on the structure of both crystalline and liquid phases is often contradictory [1-6].

Despite its apparent simplicity, methanol under the conditions of variable pressure and temperature, displays a fairly complex behavior which has not been clearly explained as yet, though it is evident that a hydrogen bond in this case plays the key structure-forming role. Whereas the weakening of hydrogen bonds in liquid methanol when heating it to high temperatures has been established quite definitely, viewpoints differ as to the pressure effect on the force of hydrogen bonds in methanol, especially at low temperatures [5,7-9]. For example, it is pointed out in [5] that the length of linear chains of liquid methanol bound by hydrogen bonds increases with pressure; however, it is established in [7] that the volume decreases due to a change in the distance between the chains, whereas their length remains unchanged. As noted in [8], under pressure there exists an appreciable interaction between the chains, which increases the force of hydrogen bonds. At the same time, following [9] the
structure of liquid methanol is not chain-like but a three-dimensional lattice and the pressure effect on liquid methanol may result from its structure disordering.

Under atmospheric pressure, methanol, with a decrease in temperature, crystallizes into a high-temperature \(\beta\)-phase at \(T=175\) K, and, with a further temperature decrease, its solid-phase transformation from the \(\beta\)- to the \(\alpha\)-phase at \(T=157\) K occurs [10-12]. The crystalline structures of \(\alpha\) and \(\beta\) modifications are determined in [8,13,14]. In the low-temperature region the methanol phase diagram was studied in a short range of pressures (up to 0.3 GPa at 77-293 K) by the DTA technique [15]. Methanol crystallizes at \(p=3.5\) GPa at room temperature, but the crystalline methanol structure cannot be unambiguously determined under high pressure (\(p>3\) GPa) [1,13,16]. The high-pressure phase of methanol is defined as a monoclinic \(\alpha\)-phase [1,13]. At the same time, in [16], a monocystal was grown in a diamond anvil cell at \(p>4\). The monocystal structure was determined as a triclinic one and the authors named it the \(\gamma\)-phase. In the pressure interval up to 0.27 GPa, the melting curves of methanol and ethanol, as well as their thermodynamic parameters during melting, are determined with a fairly high accuracy [15,19]. In ethanol, liquid-crystal phase equilibriums at higher temperatures than room temperature are studied by the volumetric method up to \(p=3.5\) GPa and interpolated into the low-temperature region to the crystallization point at atmospheric pressure [6]. Also, the Raman spectra at room temperature and pressures up to 8.2 GPa was investigated [2,17,18].

At atmospheric pressure, ethanol crystallizes to the monoclinic structure at 156 K [1,17]. Note that it is not only the type of crystalline phases but also the behavior of melting curves of methanol and ethanol that differ substantially. At low pressure, the values of the melting temperatures and their pressure derivatives for methanol and ethanol are close [15,19], whereas with the pressure increase, the difference between the melting temperatures grows and amounts to approximately 100 K at \(p=3.5\) GPa. In this case, the difference between the slopes of the melting curves \(dT_m/dp\) is about threefold [5,6].

If compressed at room temperature, ethanol crystallizes at \(p=1.9\) GPa [6]; but in doing so the kinetics of ethanol and methanol solidification under compression is rather different. Indeed, crystallization was always the case for ethanol, whereas methanol is distinguished by its capability to vitrify. At fairly high loading rates, liquid methanol can remain in an “overcompressed” state (i.e. in a supercooled state) and can vitrify at pressures of 5-10 GPa [1,16,20]. Apparently, the process of liquid methanol vitrification is encouraged by rather strong hydrogen bonds and a significant difference between the structures of the liquid and solid methanol phases. Ethanol is a material that has weaker hydrogen bonds; it features similar short-range order structures of the liquid and solid states and its vitrification was only observed at atmospheric pressure at a super-high rate of the melt cooling [20].

The nature of intermolecular forces and the physical properties of alcohols, including their elastic characteristics, are not only of great interest, but also of vital importance for experimental physics of high pressures, as both pure methanol and a methanol-ethanol mixture in the proportion 4:1 are often used as a pressure –transmitting medium that retains its hydrostatic properties up to \(p=10\) GPa [21].

The elastic properties of methanol and ethanol under pressure have been previously studied only at room temperature by the simulated Brillouin scattering procedure in a diamond anvil cell up to 6.8 GPa [22]. To our knowledge, no investigations of elastic properties of the crystalline phases of alcohols at low temperature have been carried out.

The goal of this work is: (i) to study the elastic properties of methanol and ethanol at low temperatures and high pressures with by the ultrasonic technique together with direct volume (and hence density) measurements; (ii) to construct the melting curves and the
phases transitions curves of the spirits on the basis of these measurements and compare the methanol and ethanol phase diagrams; (iii) to try to analyze the role of hydrogen bonding of the substance under discussion in there phase behaviour. The phase diagrams of methanol and ethanol are compared with the phase diagram H$_2$O ice, developed in our previous study [23,24]. It is important for comparison that H$_2$O can be considered as a system with the stronger hydrogen bonds.

**Experimental**

The measurements were carried out using a low-temperature ultrasonic piezometer in the pressure and temperature ranges up to 1.2 GPa and 90-290 K, respectively, in accordance with the procedure described in [25]. Prerefrined and dried substance was placed into a capsule representing a small thin-walled Teflon cup with a copper cap. The travel time of a longitudinal ultrasonic wave was directly measured (accurate to 0.001μs) with a MATEK equipment-based unit “Akustomer-1” designed in the Institute for High Pressure Physics of the Russian Academy of Sciences. The wave velocity in a sample was measured by transmitting a sinusoidal train of acoustic waves through the sample and the pistons of a high-pressure device. The working frequency of the unit could be varied within the range 1.7-15 MHz, with the sampling frequency of the train-forming electronic circuit being 66 MHz. The acoustic train duration was 1-4 μs. Quartz plates with a carrier frequency of 5 MHz were employed as piezosensors. In the course of experiments, changing of the ultrasonic signal travel path were also measured to an accuracy of 0.001 mm by means of displacement indicating gage. The values of the density of the sample under pressure were determined from changes in the length of the sample after closure to an initial total dimension and density of the sample.

Two series of experiments were performed and the following dependences were determined: (1) pressure dependences of the longitudinal ultrasonic wave travel time and of the sample length at constant temperature (T=const); (2) temperature dependences of the same characteristics at natural warming of the high-pressure device at constant pressure (p=const, the warming rate was 1K/min). The work resulted in obtaining baric and temperature dependences of the longitudinal wave velocity in methanol and ethanol $v_l$ (p,T) in the pressure range up to 1.2 GPa and temperature range from 90 to 290 K. Anomalies in the change of the above-mentioned characteristics were interpreted as the melting points of alcohols or as the β-α phase transition point in crystalline methanol. It is the advantage of the ultrasonic method, that it is possible to note phase transformations accompanied by small volume jumps, and continuously monitor measured parameters, determining the temperature and pressure of phase transitions with a sufficient accuracy. Altogether, more than 30 experiments were carried out for either studied alcohols.

**Results**

1. **Methanol**

The isothermal pressure dependences of the longitudinal ultrasonic wave velocity $v_l$, methanol density $\rho$, and the modulus of elongation $L=\rho v_l^2$ for crystalline and liquid phases obtained under compression of initially liquid methanol are presented in Fig.1. The lack of direct structural measurements in this work was compensated for by the data of the known structural and Raman investigations [1,13,15,16]. By comparison with the ultrasonic signal travel time and density measurements in our experiments, this made us possible to identify the observed phase transformations fairly reliably.
It should be stressed that the shear modulus for the liquid phase is zero, $G=0$, and the modulus of elongation coincides with the bulk modulus $L=B$ according to the well-known equation for the velocity of longitudinal sonic waves in isotropic media $\rho v^2 = B + (4/3)G$. The vertical dotted lines mark the pressure values corresponding to the crystallization of liquid to the $\beta$ phase and to the $\beta$-\(\alpha\) phase transition at 204 K. The liquid phase crystallization at 204 K is accompanied by the density jump $=0.030$ g/cm$^3$ ($=-3.2\%$), the change in the velocity of longitudinal ultrasonic waves by $=0.240$ km/s ($=12.6\%$), and the increase in the modulus of elongation by $=0.9$ GPa ($=26\%$). With a rise in temperature (Fig. 1, curves for $T=235$ K), the points of both phase transitions in a natural way shift to higher pressures, and the phase transitions themselves occur with smaller jumps of the measured characteristics. In this case, the density (volume) jumps become very small, and the $\beta$-\(\alpha\) phase transition can be reliably identified only from the jumps of the longitudinal wave velocity and the modulus of elongation. One should note that all considered characteristics for the \(\alpha\)-phase grow with pressure more rapidly than those for the $\beta$-phase. For example, at $T=204$ K (Fig. 1), the baric derivatives of the modulus of elongation in the $\alpha$- and $\beta$-phase are $=5.4$ and $=7.5$, respectively. It is also noteworthy that the ultrasonic velocity, the density, and the modulus of elongation for liquid methanol measured by us at room temperature are in good agreement (we are again reminded that $B=L$) with the data of [6,22].

In the second series of experiments, phase transformations resulting from the $\alpha$-phase of methanol upon warming were studied. Fig. 2 displays isobaric dependences of the same parameters as presented in the Fig.1 and obtained through the warming of crystalline

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**Fig. 1.** Typical experimental dependences of the longitudinal ultrasonic wave velocity $v_l$, density $\rho$, and the modulus of elongation $L$ for the compression of methanol at different temperatures: 204 K (the triangles), 228 K (the circles); 293 K (the squares). The vertical dotted lines correspond to the crystallization of liquid to the $\beta$-phase and the $\alpha$-$\beta$ phase transition at $T=204$ K. The short dash-and-dot lines mark the same phase transitions at $T=228$ K.

**Fig. 2.** Temperature dependences of the longitudinal ultrasonic wave velocity $v_l$, density $\rho$, and the modulus of elongation of methanol upon warming at different fixed pressures: 0.22 GPa (the squares); 0.35 GPa (the circles); 0.6 GPa (the triangles); 0.85 GPa (the overturned triangles).
methanol at different pressures. As an example, let us consider the experimental dependence \( v_l (T) \) at \( p=0.35 \) GPa. A weak variation in the temperature dependence of the longitudinal ultrasonic velocity at \( 110K<T<180K \) evidently corresponds to the \( \alpha \)-phase of methanol. Further, with a rise in temperature from 180 K to 185 K, the anomalies (i.e. the abrupt changes) of the parameters correspond to the transition to the crystalline \( \beta \)-phase, which exists in the narrow temperature range from 185 to 200 K. Next anomaly is observed at \( 200K<T<213K \) and obviously corresponds to the melting of methanol. Further, at \( T=213K \), the experimental dependences relate to the liquid phase of the studied substance. The warmings at \( p=0.35 \) GPa show the erosion and gradual vanishing of the region of existence of the \( \beta \)-phase, which can be clearly seen from the character of changes in the dependence \( v_l (T) \). It should be pointed out that with an increase in the warming pressure, diminution of the total volume jump at the \( \alpha \)-\( \beta \) and \( \beta \)-liquid phase transitions occurs, during which the densities of the \( \alpha \)- and \( \beta \)-phase of methanol are very close already at \( p=0.6 \) GPa and the pressure dependence of the density does not allow us to reveal the phase transition. It is only the temperature dependence of the velocity of longitudinal ultrasonic waves (and, accordingly, the temperature dependence of the modulus of elongation) that reveals the \( \alpha \)-\( \beta \) phase transition and proves the existence of the \( \beta \)-phase under these pressures. The \( \alpha \)-\( \beta \) phase transition is followed by a rather sharp decrease in the modulus of elongation of methanol practically at the retained density, which points to the total decrease in the bonding forces in the crystalline lattice of the \( \beta \)-phase.

The results of isobaric and isothermal experiments have permitted us to widen and substantially refine the \( p-T \) phase diagram of methanol that is shown in Fig.3 in relation to the previously known diagram [26]. Notice that the obtained experimental phase diagram of methanol agrees well with the results of [1,15,19,21], although it is much more complete. Our measurements have revealed that the region of existence of the \( \beta \)-phase of methanol
narrowed with pressure, but the $\alpha$-$\beta$-phase transition and the $\beta$-phase melting can be separated up to 1.2 GPa in the least.

It should be further pointed out that the melting curve of methanol flattens out at $p>0.75$ GPa. For example, such flattening is not observed for ethanol (see the next subsection). In accordance with the Clapeyron-Clausius equation, taking into account that the liquid phase density is lower than the density of the corresponding crystal near the melting curve, such behavior can be associated with a larger compressibility of liquid methanol or with an additional densification of the liquid phase structure of methanol (at $p\approx0.6-0.7$ GPa near the melting curve) as a result of changes in the short-range structure of the liquid.

To support the latter assumption, experimental data has been obtained. Indeed, weak anomalies in the ultrasonic wave velocity and in the density were found in the liquid phase of methanol in experiments on its warming in the 0.1-0.4 GPa pressure range and were observed in the 230-250 K temperature range. The temperature dependences of the density and of the modulus of elongation of liquid methanol at $p=0.35$ GPa are presented in Fig. 4 on an enlarged scale. Notice that the anomalies, despite their small values, feature stable behavior and recurrence, and their amplitudes exceed the precision of relative measurements. The points of the observed anomalies were plotted on the phase diagram of methanol (Fig. 3) and fell in a fairly narrow region which may be hypothetically regarded as a boundary separating the two structural types of liquid methanol, namely, with a higher and a lower density of molecular packing. It should be mentioned that the position of this tentative boundary agrees well with the beginning of the melting curve flattening. Naturally, the above conclusions and assumptions are preliminary and call for further studies, although the very fact of the presence of anomalies in liquid methanol has been established with a comparatively high certainty.

2. Ethanol

The baric dependences of the longitudinal ultrasonic wave velocity $v_l$, density $\rho$, and the modulus of elongation $L$ for the crystalline and liquid phases of ethanol obtained in the experiments are presented in Figs. 5. Fig. 5 shows the data obtained at three different temperatures. The group of dependences for $T=293$ K refers to liquid ethanol, whereas the dependences at $T=218$ K and 190 K indicate a phase transition from the liquid to crystalline state which was observed at $p=0.98$ GPa and $p=0.28$ GPa, respectively. At $T=190$ K, the phase transition from the liquid to crystalline state occurs with the jump of density $\approx0.016$ g/cm$^3$ ($\approx1.7\%$), an abrupt change in the longitudinal ultrasonic waves velocity by $\approx0.425$ km/s ($\approx22\%$), and the increase in the modulus of elongation by $\approx1.78$ GPa ($\approx49\%$). The temperature rise does not lead to any significant changes of the jumps in the dependences $v_l$ and $L$, as distinct from what is observed for methanol.

![Fig. 5. Typical experimental dependences of the longitudinal ultrasonic wave velocity $v_l$, density $\rho$, and the modulus of elongation $L$ for the compression of methanol at different temperatures: 190 K (the circles); 218 K (the triangles); 293 K (the squares).](image-url)
agrees with the behavior of the melting curves of alcohols under study. The velocities of longitudinal ultrasonic waves, the density, and the modulus of elongation (in this case, the bulk modulus as well) of ethanol measured at room temperature (Fig. 5) agree well with the data of [23]. Isobaric dependences of density and elastic characteristics obtained from the warming of crystalline ethanol at different pressures give the similar strong anomalies in the change of density and longitudinal ultrasonic wave velocity, being evidently caused by the melting of ethanol. It is noteworthy that the instant when the substance becomes completely liquid is more clearly appeared for methanol than for ethanol, which might be associated with the fact that the structures of liquid and crystalline ethanol are similar, whereas the structures of liquid and solid states of methanol differ greatly, as indicated in [1]. The ethanol phase diagram constructed on the base of our experimental data is presented in Fig. 6 and is in good agreement with the results of [1, 16, 19] and the reference information of [26]. It should be remarked that in liquid ethanol, as distinct from methanol, the baric and temperature dependences of ultrasonic velocities have no anomalies.

3. Phase diagram of \( \text{H}_2\text{O} \) ice

Previously [23, 24], we have made the detailed ultrasonic study of the low-temperature nonequilibrium (transitional) phase diagram of \( \text{H}_2\text{O} \) ice in the pressure range 0-1.7 GPa and temperature range 77-200 K (Fig. 7). A continuous crossover from the thermodynamically driven Ih-II transition to the nonequilibrium scenario of solid state amorphization Ih-hda (high density amorphous) through the intermediate I-IX transition was clearly observed for pressurized ice Ih at the temperature decrease. The Ih-IX transition was detected by the abrupt shift of IX-VI transition toward lower pressures with respect to the II-VI transition in accordance with the thermodynamic trend. Elastic softening was established to be the common precursor for the solid state amorphization Ih-hda and transformation between the low and high density amorphous (lda and hda) phases of ice. Three distinct stages (shear elastic softening, bulk softening, and main volume jump) were found for the temperature-
induced hda-lda transformation. The detailed picture of amorphous-amorphous transformations showed their complicated nonergodic nature combining the features typical for both the first-order transition and singularity-free scenario.

Discussion and conclusions

In this work, we used a low-temperature high-pressure ultrasonic piezometer [25] for the first time to study liquids. Combination of the ultrasonic technique with the direct measurement of density of substances in the experiments under pressure has proved sufficiently effective for the investigation of phase diagrams of substances in solid and liquid states. In particular, the α-β phase transition of methanol can be better found from the dependences of ultrasonic velocities, whereas the melting point of crystalline β-methanol can be more accurately established from the density curves (see for both phase transitions the dependences of the corresponding characteristics for p=0.6 GPa and p=0.85 GPa in Fig.2).

Thus, the p-T phase diagrams of methanol and ethanol have been studied in this work in a fairly wide range of pressures and temperatures (up to 1.2 GPa and 90-290 K), and elastic properties of the crystalline and liquid phases of methanol and ethanol have been examined by using the ultrasonic method. This has resulted in a more precise determination of the phase diagrams of methanol and ethanol, including the stability regions of crystalline phases and positions of the melting curves. The phase diagram of ethanol is rather simple in the pressure range under investigation. On the whole, the experimental data supports the view of ethanol as a system with weak hydrogen bonds. Unlike ethanol, methanol displays a much more complex behavior and a more complex phase diagram. Within the framework of this investigation, the interval of pressures for the crystalline methanol melting curve and for the α-β phase transition line has been substantially widened (Fig.3). The extrapolation of the lines of these phase transitions (Fig.3) into the region of higher pressures shows that the stability region of the β-phase methanol evidently ends up at p~1.5 GPa. However, it still remains unclear whether the α-β liquid triple point exists. Our measurements indicate that such a point is more likely to exist at approximately p=1.4 GPa, because the possible γ-phase [16] or any other possible high-pressure phase are apparently stable at notably higher pressures. However, to solve this question, direct experiments at p>1.2 GPa are necessary.

It is of interest to compare the characteristics of liquid methanol and ethanol, which is done in Fig. 8 for room temperature. Lower baric derivatives of the modulus of elongation (coinciding with the bulk modulus for the liquid state) of the methanol phases as opposed to ethanol is indicative of the crystalline lattice softening, with the increase of the softening at p>0.5 GPa. In this case, it is important that the density of methanol grows with pressure more rapidly and becomes higher than the density of ethanol. As was already pointed out above (subsection 2.1), higher compressibility of methanol can cause flattening of its melting curve, and Fig. 8 supports this standpoint. It remains unclear to what extent a higher compressibility of methanol can be linked to a possible reorganization of the short-order structure in the liquid, or else the difference in compressibility of the two alcohols arises from a specific character of the intermolecular interaction and hydrogen bonds.

An important observation first made in the present work is the fact that an additional and rather sharp densification of the methanol melt occurs in the ranges of pressures 0.2-0.6 GPa and temperatures 230-250 K (Fig.4), though the amplitude of this anomaly is not large. This densification is probably associated with structural changes in the liquid phase. It is of interest that a small increase in the liquid density is accompanied with a decrease in the bulk modulus, which is rather unusual and seems more likely to be the exception to the rule. Nevertheless, such anomalous behavior (a decrease in the bulk modulus at the positive density jump) were earlier observed in the systems with hydrogen bonding, in particular, at the phase transition between 1h and III crystalline phases of H2O ice [27]. A still brighter example of such an anomaly was observed for D2O ices [28], where the hda high density
amorphous ice, being the densest phase, had the bulk modulus appreciably lower than the corresponding bulk moduli of the lda low density amorphous ice and the 1h and 1e crystalline phases. We emphasize that the given above example of the comparison of the lda and hda disordered ices is extremely important for our case, because the considered system, i.e., liquid methanol, is a disordered system as well.

From low-temperature data on Raman scattering, it is possible to suggest that a rather abrupt transition from the quasi-chain-like structure of a liquid to the branched net structure with the participation of several hydrogen bonds per molecule occurs in the process of liquid methanol densification near the melting curve. It should be remarked that at p>0.7 GPa, the compression of liquid methanol at room temperature also causes the structural evolution associated with changes in the cluster structure of the melt [2]. The earlier investigations of the density and elastic properties of liquid methanol and ethanol under pressure [22] did not, because of a low experimental accuracy, allow one to reveal the difference in the behavior of these substances under compression. Measurements of the density and elastic characteristic of crystalline and liquid alcohols in a fairly wide range of pressures and temperatures conducted in this work will make it possible to verify various theoretical models and to elucidate to a considerable degree the behavior of hydrogen bonds in simple alcohols at the change in thermodynamic parameters.

For methanol, we have established the exact boundary of the α-β crystal-crystal phase transition and found a week anomaly of density and longitudinal ultrasonic velocity in the liquid phase at temperatures 230 to 250 K and pressures 0.2 to 0.6 GPa, which is likely can be associated with the structural changes to the more dense liquid phase with the increase of pressure. Still, there is questionable an existence of the α-β-liquid triple point. A nature of structural changes in the liquid phase should also be clarified by direct in situ methods. In general, methanol demonstrates more complicated phase behavior under pressure in contrast to ethanol, phase diagram of which is quite simple in the studied pressure-temperature area. We associate the differences in the phase diagrams of methanol and ethanol to the stronger hydrogen bonds in methanol and to simpler structure of its molecules. The last trend is directly illustrated by H2O water, which has one of the simplest molecule, the strong hydrogen bonding, and quite complicated phase diagram. The extension of pressure and temperature intervals of the experimentally studied thermodynamic (equilibrium) and transitional diagrams of methanol, ethanol, and H2O ice will provide further insight into high-pressure properties of hydrogen-bonded solid systems.

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Literature