# Study of the acoustic and thermodynamic properties of 2-methyl-2,4-pentanediol by means of high-pressure speed of sound measurements

Magdalena Cempa, Marzena Dzida, Edward Zorębski[1]

*Institute of Chemistry, University of Silesia, 40-006 Katowice, Poland, [1]Email: emz@ich.us.edu.pl*

## Introduction

The experimental data of thermodynamic properties under elevated pressures are of considerable interest from both fundamental and practical point of view. In particular, it refers to associating liquids, which are key substances in the chemical industry. Because of the relation between thermodynamic properties, only some of them can be measured under high pressure (the others can be calculated using the experimental results). One of the more convenient and well–established methods for the determination of the thermodynamic properties under elevated pressures, where direct measurements are extremely difficult, is the acoustic method. This method is based on the measurements of the speed of sound as a function of temperature and pressure. In the studied temperature-pressure range the dispersion phenomena must be obviously absent. Additionally, the density and isobaric heat capacity measured as a function of temperature at atmospheric pressure are needed. The detailed description of the calculation algorithm can be found elsewhere [1,2].

## Experimental

2-Methyl-2,4-pentanediol (purity > 99 %) used in this study was supplied by Aldrich and used without further purification. However, each sample was degassed in an ultrasonic cleaner just before the all measurements. The speed of sound was measured using two measuring sets constructed at the University of Silesia. At atmospheric pressure, the speed of sound at a frequency of 2.1 MHz was measured in the temperature range from (286 to 318) K. Under elevated pressures, the speed of sound at a frequency of 2 MHz was measured in the temperature range from (293 to 318) K. The measuring sets operate on the basis of the pulse-echo-overlap method. More details can be found in the previous publications [3,4,5]. The uncertainty was estimated to be better than ±0.5 $m\cdot s^{-1}$ and ±1 $m\cdot s^{-1}$ at atmospheric pressure and at elevated pressures (up to 101 MPa), respectively. The density under atmospheric pressure was measured using a vibrating tube densimeter (DMA 5000, Anton Paar). The isobaric heat capacity under atmospheric pressure was measured by means of a differential scanning calorimeter Micro DSC III. The uncertainties of the measurements were estimated to be better than ± 0.05 $kg\cdot m^{-3}$ and to be of ±0.25 % for the density and heat capacity, respectively. All experimental data have been reported in [6].

## Results and discussion

The speeds of sound are plotted as function of temperature and pressure in Figs 1 and 2, respectively. For a given pressure, the speed of sound decreases almost linearly with increasing temperature (an increase of the pressure produces a slight decrease of the slope of these curves). The pressure dependencies are evidently non-linear and with increasing pressure its effect on the speed of sound gradually decreases. Both temperature and pressure dependencies are typical for liquids.

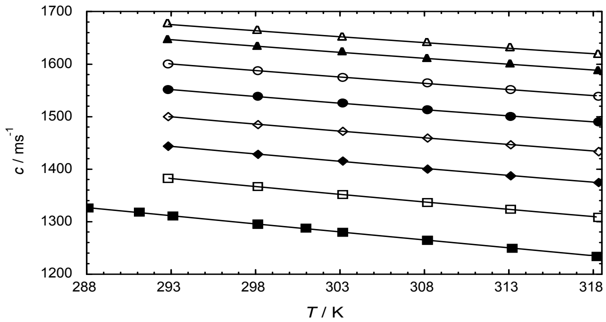


**Figure 1**: Speed of sound as a function of temperature for 2-methyl-2,4-pentanediol at the pressures: ■, 0.1 MPa; □, 15.20 MPa; ♦, 30.39 MPa; ◊, 45.49 MPa; ●, 60.79 MPa; ○, 75.99 MPa,; ▲, 91.18 MPa; Δ, 101.32 MPa. Lines – second order polynomials.

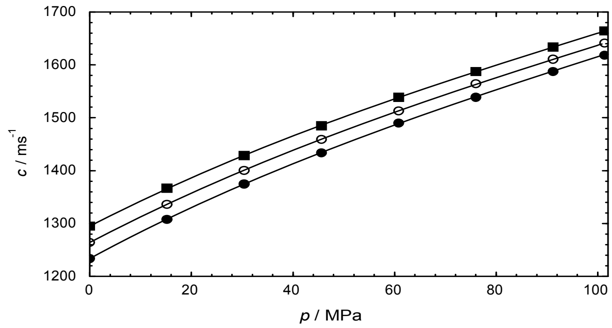


**Figure 2:** Speed of sound as a function of pressure for 2-methyl-2,4-pentanediol at the temperatures: ■, 298 K; o, 308 K; ●, 318 K. Lines – second order polynomials.

The acoustic impedance, *Z*, is a property causing resistance of the propagation of ultrasound wave. It was calculated by the following relationship:

$$Z = \rho \cdot c \qquad [kg\cdot m^{-2}\cdot s^{-1}] \qquad (1)$$

where $\rho$ is density and *c* is speed of sound. As expected, the acoustic impedance increases with increasing pressure and decreasing temperature, as can be seen in Figs 3 and 4.

One of the very interesting properties, that can be calculated using the acoustic method, is the internal pressure. The internal pressure $P_{int}$ was calculated from the relation:

$$P_{int} = T \cdot \alpha_p \cdot \kappa_T^{-1} - p \qquad [MPa] \qquad (2)$$

where

$$\kappa_T = (\rho \cdot c)^{-2} + \alpha_p^2 \cdot T \cdot (\rho \cdot c_p)^{-1} \qquad [MPa] \qquad (3)$$

and $\kappa_T$ is isothermal compressibility, $\alpha_p$ is isobaric thermal expansibility, and $c_p$ is isobaric heat capacity. The results are plotted in Figs 5 and 6 (numerical data can be found in [6]).

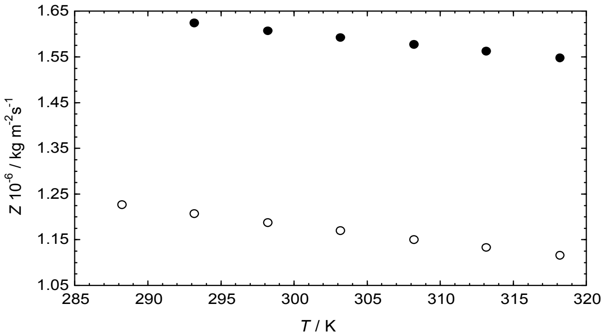


**Figure 3:** Acoustic impedance as a function of temperature for 2-methyl-2,4-pentanediol at the pressures: o, 0.1 MPa, and ●,100 MPa.

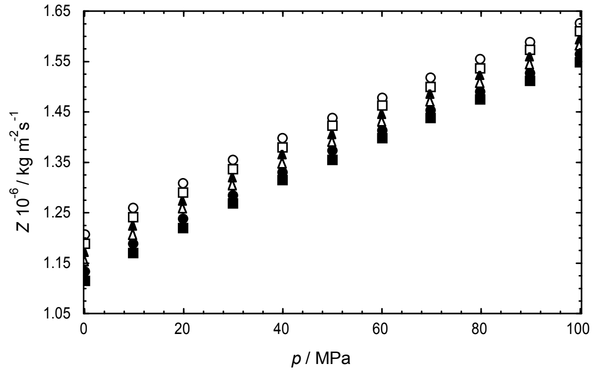


**Figure 4:** Acoustic impedance as a function of pressure for 2-methyl-2,4-pentanediol at the temperatures: o, 293.15 K; □, 298.15 K; ▲, 303.15 K; Δ, 308.15 K; ●, 313.15 K; and ■, 318.15 K.

It is observed that the internal pressure decreases linearly with increasing temperature along isobars up to 30 MPa. The internal pressure is temperature independent at ca. 40 MPa. At higher pressures, the internal pressure increases with increasing temperature along isobars. It means that the isotherms of $P_{int}$ of 2-methyl-2,4-pentanediol cross each other at ca. 40 MPa. The internal pressures as function of pressure show maxima. With increasing temperature the maxima of $P_{int}$ move towards higher pressures, i.e., for $T$ = 293.15 K the maximum lies about 10 MPa, whereas for $T$ = 318.15 K the maximum lies about 25 MPa.

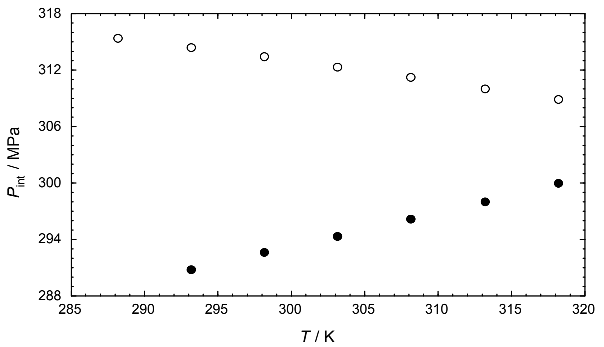


**Figure 5:** Internal pressure as a function of temperature for 2-methyl-2,4-pentanediol at the pressures: ○, 0.1 MPa and ●, 100 MPa.

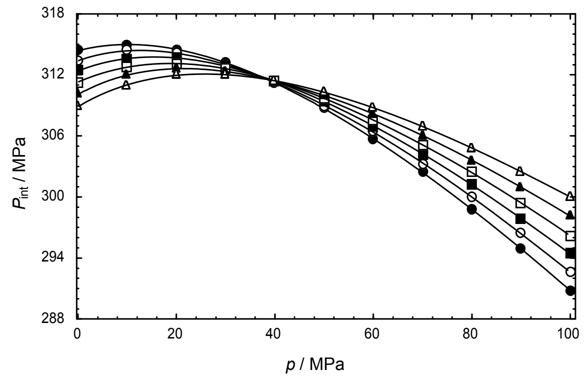


**Figure 6**: Internal pressure as a function of pressure for 2-methyl-2,4-pentanediol at the temperatures: ●, 293.15 K; o, 298.15 K; ■, 303.15 K; □, 308.15 K; ▲, 313.15 K; and Δ, 318.15 K. Lines - $P_{int} = \sum_{i=0}^{3} a_i (p/100)^i$.

Such pressure-temperature dependence of $P_{int}$ is typical for 1-alkanols [7]. This results suggest that the network structure of 2-methyl-2,4-pentanediol is predominantly formed by intermolecular H-bonds and intramolecular H-bonds play minor role. However, the steric hindrance disturbs not only the formation of intramolecular H-bonds, but also the formation of intermolecular H-bonds. The existence of the side chain methyl group affects also strong pressure dependence of the isentropic and isothermal compressibilities [6].

## Literature

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