



**Acoustics'08
Paris**
June 29-July 4, 2008

www.acoustics08-paris.org

measurements under high pressure of ultrasonic velocity in glycerol

Hassina Khelladi^a, Frédéric Plantier^b, Jean Luc Daridon^b and Hakim
Djelouah^a

^aFaculty of Physics, University of Science and Technology Houari Boumedienne, BP 32 El
Allia, Bab-Ezzouar, 16000 Algiers, Algeria

^bUniversité de Pau et des Pays de l'Adour, Laboratoire des Fluides Complexes, UMR 5150,
BP 1155, 64000 Pau, France
hassinakhelladi@yahoo.fr

Glycerol has been the subject of significant scientist interest. Indeed, glycerol is a polyalcohol and the presence of three hydroxyl groups per molecule makes glycerol a complex system to explore. The purpose of this investigation is to measure under high pressure the ultrasonic wave velocity in glycerol, from which a number of important thermodynamic properties could be derived and determined as a function of pressure and temperature. Pressure and temperature ranges exploited in this experimental investigation of various glycerol properties, are extended respectively from 0.1MPa to 100MPa and from 10°C to 100°C. A high pressure measurement cell equipped with temperature and pressure monitoring and control instrumentation is used. A time of flight method is exploited to measure, under high pressure, the ultrasonic wave velocity at different temperatures. The resulting experimental data of ultrasonic wave velocity in glycerol combined with measurements at atmospheric pressure, of density, specific heat and thermal expansion coefficient are used to derive density at elevated pressures. As isentropic compressibility is linked to ultrasonic wave velocity and density by means of the Newton-Laplace equation, this intrinsic physical property is easily deduced. These results led to the behavior of each property as a function of temperature and pressure.

1 Introduction

Glycerol is used in nature as a cryoprotectant and has been the focus of study by researchers in cryopreservation. Indeed, the cryonics is to cryopreserve humans (kidneys, brains...) so that future technology may one day restore those people to a disease free and aging free life... The means to this end is to reduce or eliminate the damage caused to tissues by freezing water. Cryoprotectants (anti-freeze agents) are the usual means to eliminate ice crystals, where high pressure is needed to assist some cryoprotectant in the cryopreservation of some tissues [1].

As a lack of data concerning glycerol at elevated pressure is observed, measurements under high pressure of the ultrasonic wave velocity in glycerol and versus temperature are carried out, from which a number of important thermodynamic properties could be derived and determined as a function of pressure and temperature.

The resulting experimental data of ultrasonic wave velocity in glycerol combined with measurements at atmospheric pressure, of density, specific heat and thermal expansion coefficient are used to derive density at elevated pressures.

As isentropic compressibility is linked to ultrasonic wave velocity and density by means of the Newton-Laplace equation, this intrinsic physical property is easily deduced.

These results led to the behavior of each property as a function of temperature and pressure.

2 Experimental devices

The high pressure equipment is composed of a piston, which can move in the measurement cell allowing the transmission of the appropriate static pressure to the studied fluid via the compression oil. The system could reach pressures up to 100 MPa and with a temperature range from 283.15 K to 373.15 K. The measurement cell is completely immersed in a silicone oil bath whose temperature is controlled by a thermostat in immersion, operating in a temperature range from 243.15 K to 473.15 K. The homogenization of the bath is ensured by pulsed air sprays. The tank also has a cooling coil intended to improve the regulation at temperatures close to the ambient temperature. The tank itself consists of a double wall where a polyurethane expansive foam was flowed in order to minimize the thermal losses to external medium. A platinum probe Pt 100 is placed so that the temperature

measurement is representative of that inside the studied sample and the precision of the temperature values is better than 0.1 K [2]. A piston, playing the role of an interface between the sample and the compression oil inside the cell, transmits the pressure to the studied fluid by avoiding any contact between the two fluids. The pressure measurement is carried out by means of a sensor connected to the exit valve of the cell. The measurement precision is estimated to 0.1% on the investigation range [2].

A device is constructed as an ultrasonic sample-holding to be inserted into the high pressure cell. The acoustic probes are composed of two piezoelectric transducers (PZT) with a diameter of 12 mm, a resonance frequency of 5 MHz and placed facing each other at a distance of about 3 cm. The pulse technique is used to measure the ultrasonic velocity since it is more suitable for high pressure conditions. For that purpose, a pulser-receiver (PANAMETRICS, model 5055 PRM) is used.

From the transit time measurements or the time delay between a pair of echoes received by the acoustic probe, the ultrasonic velocity by which the ultrasound wave propagated through the glycerol sample at a given condition is determined. The ultrasonic velocity is given by the ratio of the known acoustic path length to the transit time, where acoustic path is double the direct straight path length. A correction of the sample length has been made by taking into account the thermal expansion coefficient and the compressibility coefficient of the construction material which compose the transducer holder. The determination of the infinitesimal ultrasonic wave velocity is tainted with an inaccuracy lower than 0.1% [2].

The density determination is carried out in two steps. First, the densities are measured at atmospheric pressure in the same interval of temperature as the ultrasonic wave velocity measurement, by using a vibrating U-tube densitometer (Anton Paar, model DMA 60) with an accuracy of 0.01%. The U-shaped tube, which contains the glycerol sample, is excited to undamped oscillation.

The temperature in the tube cell is measured with a standard temperature probe Pt 100 coupled with a digital display (AOIP, model PN 5207). A Julabo thermostatic bath with silicone oil as circulating fluid is used in the thermostat circuit of the measuring cell makes possible the control of the temperature at about the hundredth of degree.

The density ρ is deduced from the period of oscillation Λ of the vibrating tube as follows [2]:

$$\rho(P_0, T) = A(T)\Lambda^2 + B(T, P) \quad (1)$$

A and B are the apparatus constants determined by the calibration method suggested by Lagourette et al. [3] and by measuring, for each temperature, Λ_1 and Λ_2 the oscillation periods of two reference fluids of known densities ρ_1 and ρ_2 . The chosen fluids as standard of calibration is water, for which sufficiently accurate data are presented in the work of Kell et al. [4], and the vacuum obtained by using an auxiliary vacuum pump allowing to reach a pressure lower than 10^{-4} MPa. The absolute uncertainty on the densities determination is lower than $3 \cdot 10^{-5}$ g/cm³ [2].

The second step is based on the experimental results obtained in the first step. Indeed while referring to Davis et al. work [5], it is possible by the means of the ultrasonic wave velocity measurement under pressure at various temperatures, to determine numerically the density under pressure knowing the density and the specific heat at atmospheric pressure.

Indeed, a relation linking the density variation to an isothermal variation of the pressure can be established [4-6]:

$$d\rho = \left(\frac{1}{c_0^2} + \frac{T\alpha_p^2}{c_p} \right) dP \quad (2)$$

In this expression c_0 indicates the ultrasonic velocity, α_p is the isobaric expansion coefficient, T is the absolute temperature and c_p represents the specific heat at constant pressure.

Therefore, the integration of the equation (2) with respect to P leads to the following relationship [2, 4-8]:

$$\rho(P, T) = \rho(P_{atm}, T) + \int_{P_{atm}}^P c_0^{-2} dP + T \int_{P_{atm}}^P (\alpha_p^2 / c_p) dP \quad (3)$$

$\int_{P_{atm}}^P c_0^{-2} dP$ is integrated analytically by smoothing, versus the pressure and the temperature, the square reverse of the measured values of the ultrasonic velocity by the method of least squares [2, 4]. The average absolute relative deviation observed between the expectations of this smoothing function and the experimental data is lower than 0.02% [2].

A "predictor corrector" algorithm elaborated by Daridon et al. [6, 7] makes possible to evaluate the following term $\int_{P_{atm}}^P T(\alpha_p^2 / c_p) dP$. The developed algorithm is based on

an iterative approach which initially adopts Denielou et al [9] routine and the obtained values from the first iteration are corrected by using Davis et al. [5] scheme. The corrective process is then repeated until the computed values remain invariant. It should be noted that the c_p values, at atmospheric pressure, result from Zabransky et al. [10] work, which the reported data are known with a precision of 1% and the interpolation by a third degree polynomial of $\rho(P_{atm}, T)$ makes possible to have the initial estimation of the isobaric expansion coefficient α_p .

The comparison of the obtained under pressure density data with those resulting from Cibulka et al. [11] compilation

related to glycerol attests the precision of the achieved values since the average absolute relative deviation is lower than 0.2%.

3 Results and discussion

The glycerol or the glycerine, $C_3H_8O_3$, is a polyalcohol of the form $(C_nH_{2n+2}O_n)$. Its scientific denomination is the propan -1,2,3- triol (or -1,2,3- propanetriol). The glycerol used in the experiments is a SIGMA-ALDRICH (Glycerol 99.5 + %, water max 0.5 %, ignition residue max 0.005 %) product, employed without any further purification.

The pressure and temperature ranges exploited in this experimental investigation of various glycerol properties, are extended respectively from 10 °C to 100 °C and from 0.1 MPa to 100 MPa. For each isotherm, the pressure step of two consecutive measurements is 10 MPa. When the isotherm is entirely covered, the temperature value is increased by 10 °C step. Once the thermal equilibrium reached, the same experimental measurements are carried out to the new isotherm. Measurements in pressure are taken once pressure stability is established. It should be pointed out that the operational mode, of how the measurements are taken, has the advantage to reduce considerably the necessary time to come back to the thermodynamic equilibrium.

3.1 Ultrasonic wave velocity

The infinitesimal ultrasonic wave velocity in glycerol shows a monotonous behavior of c_0 versus the temperature and the static pressure (Fig. 1). The lowest value of the infinitesimal ultrasonic wave velocity in glycerol (1741.03 m/s) corresponds to the highest temperature and the lowest static pressure. Inversely, the highest value of the infinitesimal ultrasonic wave velocity in glycerol (2153.36 m/s) corresponds to the lowest temperature and the highest static pressure.

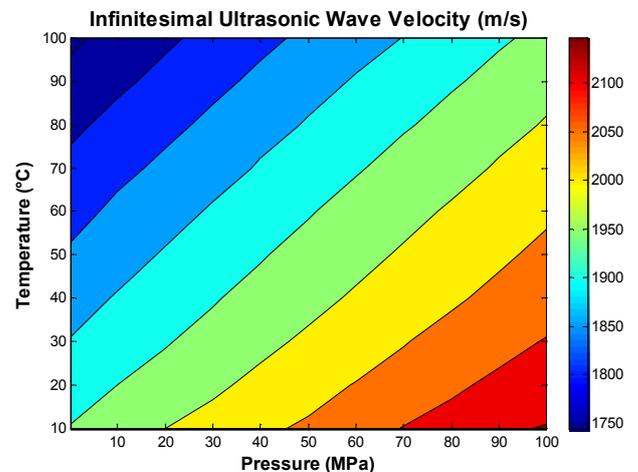


Fig. 1 Infinitesimal ultrasonic wave velocity of glycerol versus temperature and static pressure

3.2 Density

The glycerol density shows a monotonous behavior of ρ_0 versus the temperature and the static pressure (Fig. 2). The lowest value of the glycerol density (1209.27 kg/m^3) corresponds to the highest temperature and the lowest static pressure. Conversely, the highest value of the glycerol density (1291.01 kg/m^3) corresponds to the lowest temperature and the highest static pressure.

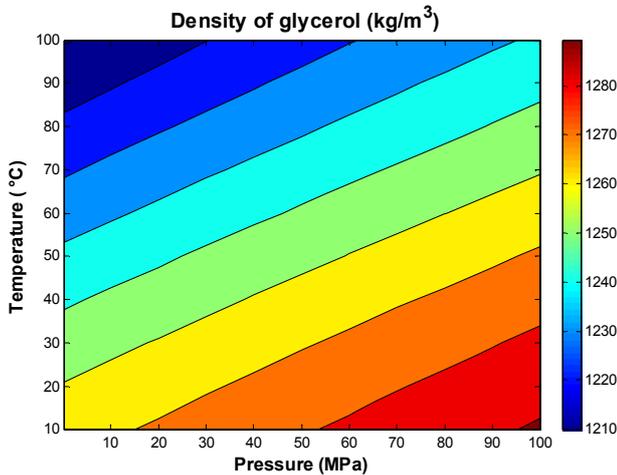


Fig. 2 Density of glycerol versus the temperature and the static pressure

3.3 Adiabatic compressibility coefficient

The amount of contraction is governed by the compressibility, which is dependent on the intermolecular forces acting within the analyzed fluid. Thus, compressibility is an important property determined by the balance between attractive and repulsive forces and enters into many pressure dependent thermodynamics expressions. The isentropic compressibility is linked to ultrasonic wave velocity and density by means of the Newton-Laplace equation [12]:

$$\chi_s = \frac{1}{\rho_0 c_0^2} \quad (4)$$

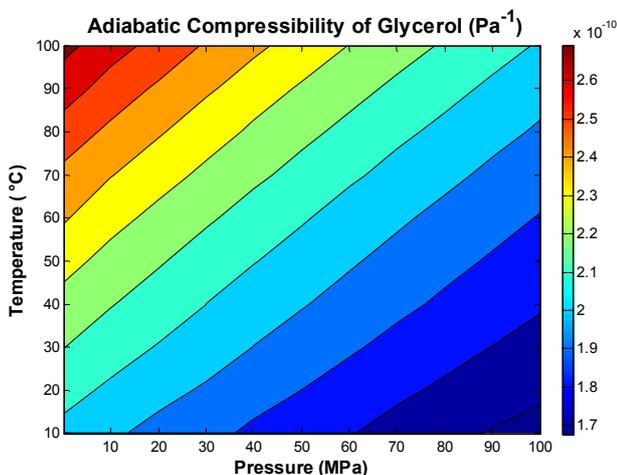


Fig. 3: Adiabatic compressibility of glycerol versus the temperature and the static pressure

The adiabatic compressibility coefficient in glycerol shows a monotonous behavior of χ_s versus the temperature and the static pressure (Fig. 3). The lowest value of the adiabatic compressibility coefficient in glycerol ($0.167(\text{GPa})^{-1}$) corresponds to the lowest temperature and the highest static pressure. Conversely, the highest value of the adiabatic compressibility coefficient in glycerol ($0.273(\text{GPa})^{-1}$) corresponds to the highest temperature and the lowest static pressure.

4 Conclusion

The obtained measurements of some glycerol properties, under static pressure and at various temperatures, constitute a database which can provide in the future a useful tool to test liquid state theory.

The complex nature of glycerol, which makes it such an interest subject for research, also makes it difficult to simulate. As computer simulation is powerful tool for the study of structure and dynamics in glycerol, future studies will concentrate on the effect of pressure on structure and hydrogen bonding in glycerol by using molecular simulation.

Acknowledgements

The first author would like to thank the organizing societies as well as the acoustics' 08 Paris conference for the offered grant in order to participate at the acoustics' 08 Paris conference.

References

- [1] P. Masson, C. Tonello, C. Balny, "High pressure biotechnology in medicine and pharmaceutical science", *Journal of Biomedicine and Biotechnology* 1:2, 85-88 (2001).
- [2] F. Plantier, J. L. Daridon, B. Lagourette, "Measurement of the B/A nonlinearity parameter under high pressure: Application to water", *J. Acoust. Soc. Am.* 111, 707-715 (2002).
- [3] B. Lagourette, C. Boned, H. Saint Guirons, P. Xans, H. Zhou, "Densimeter calibration method versus temperature and pressure", *Meas. Sci. Technol.* 3 699-703 (1992).
- [4] G. S. Kell, E. Whalley, "Reanalysis of the Density of liquid water in the range 0-150°C and 0-1kbar", *The Journal of Chemical Physics* 62, 3496-3503 (1975).
- [5] L. A. Davis, R. B. Gordon, "Compression of mercury at high pressure", *The Journal of Chemical Physics* 46, 2650-2660 (1967).
- [6] J. L. Daridon, B. Lagourette, "Mesure de la vitesse ultrasonore sous haute pression pour la caractérisation thermophysique d'un mélange ternaire", *Acustica. Acta acustica* 82, 32-38 (1996).
- [7] J.L. Daridon, B. Lagourette, P. Xans, "Thermodynamic properties of liquid mixtures containing gas under

- pressure based on ultrasonic measurements”, *Fluid Phase Equilibria* 100, 269-282 (1994).
- [8] F. Plantier, J. L. Daridon, B. Lagourette, “Measurement of the acoustic nonlinearity parameter in liquid alkanes under pressure and comparison with the Lee Kesler correlation”, *High Temperatures- High Pressures* 35/36, 109-116 (2003/2004).
- [9] L. Deneliou, J. P. Petitet, C. Tequi, G. Syfosse, “Mesure de la vitesse du son sous pression dans les silicates liquides, Mise au point de la méthode sur un sel fondu”, *Bull. Minéral* 106,139-146 (1983).
- [10] M. Zabransky, J.V. Ruzicka, V. Majer, E.S. Domalski, “Heat Capacity of Liquids: Critical Review and Recommended Values. Volume I et II”, *J.Phys.Chem.Ref.Data* 6 (1996).
- [11] I. Cibulka, L. Hnedkovsky, T. J Takagi, “P- ρ -T Data of liquids: Summarization and evaluation. 4 higher 1-alkanols (C11, C12, C14, C16), secondary, tertiary, and branched alkanols, cycloalkanols, alkanediols, alkanetriols, ether alkanols, and aromatic hydroxy derivatives”. *Chem. Eng. Data* 42, 415-433 (1997).
- [12] N. Nolting, “Relation between adiabatic and pseudo-adiabatic compressibility in ultrasonic velocimetry”, *J. Theo. Biol.* 175, 191-196 (1995).