Acoustic Method as a Precise Tool for Determining pVT Data of Liquids

Marzena Dzida[1, S, C] and Małgorzata Musiał[2]

[1]*Institute of Chemistry, University of Silesia in Katowice, Katowice, Poland*
[2]*Applied Chemicals and Materials Division, National Institute of Standards and Technology, Boulder, CO, U.S.A.*
marzena.dzida@us.edu.pl

High-pressure thermodynamic properties of liquids are of considerable interest from the fundamental and practical points of view. Their knowledge allows better understanding of the type and nature of the intermolecular interactions, thus developing adequate models of the liquid state. The high-pressure data help in developing technologies that require working liquids exposed to changing pressure, e.g., those of fuels, refrigerants, hydraulic fluids, cleaning and foaming agents, etc. The acoustic method has found acceptance as a precise tool for the determination of thermodynamic properties of compressed liquids. The speed of sound is the thermodynamic equilibrium property u_0 (*i.e.,* it can be used in the Laplace-Newton equation), first, at low frequencies, where the speed of sound does not depend on frequency, and, secondly, the effects of absorption on the speed of sound are small, *i.e.,* the dissipative processes are neglected [1]. With the exception of liquids that show rotational isomerisms [2,3], the ultrasound velocity dispersion in organic liquids occurs usually at frequencies above those used in speed of sound measurements. Thus, the speed of sound that is determined with available equipment is mostly the thermodynamic one. However, some ionic liquids exhibit dispersive effects at a relatively low frequency range. Thus, the speed of sound measured with available equipment is a non-thermodynamic speed and cannot be used for determining volume as a function of pressure and temperature (*pVT* data) and related quantities. IUPAC recommended "…the interpretation of speed-of-sound values and their usability for the determination of related thermodynamic properties can only be done when the absorption coefficient or relaxation regions are known..."[4] based on our work [1] as "Good Research Practice because it may require additional measurements for complete characterization of the system" [4]. The *pVT* data obtained from the thermodynamic speed of sound belong to the most reliable ones because the speed can be measured accurately over a wide range of temperature and pressure. Moreover, the acoustic method is based on the speed of sound measurements as a function of temperature and pressure and then integration of the isothermal compressibility with respect to pressure. In turn, the densimetric method is based on measuring the density as a function of temperature and pressure and then calculating the other properties by differentiation with respect to temperature and pressure. Thus, the first approach seems to be more reliable because integrations are generally more accurate than numerical derivatives.

Other affiliations of Małgorzata Musiał: Institute of Chemistry, University of Silesia in Katowice, Katowice, Poland; and Department of Physics, University of Colorado, Boulder, CO, United States

References

1. M. Dzida, E. Zorębski, M. Zorębski, M. Żarska, M. Geppert-Rybczyńska, M. Chorążewski, J. Jacquemin, I. Cibulka, Chem. Rev. 2017, 117, 3883.
2. K. F. Herzfeld, T. A. Litovitz, Absorption and Dispersion of Ultrasonic Waves; Academic Press: New York and London, 1959.
3. E. Wilhelm, J. Sol. Chem. 2010, 39, 1777.
4. A. Bazyleva et al., Pure Appl. Chem. 2021, 93, 253.