International Journal of Thermal Sciences 90 (2015) 62–69

Contents lists available at ScienceDirect

International Journal of Thermal Sciences

journal homepage: www.elsevier.com/locate/ijts

Thermal properties of compressed liquids: Experimental determination via an indirect acoustic technique and modeling using the volume fluctuations approach

Mirosław Chorążewski [a], [*], Eugene B. Postnikov [b]

[a] Institute of Chemistry, University of Silesia, Szkolna 9, 40-006 Katowice, Poland
[b] Department of Theoretical Physics, Kursk State University, Radishchevast., 33, 305000 Kursk, Russia

A R T I C L E I N F O

Article history:
Received 23 July 2014
Received in revised form
23 November 2014
Accepted 24 November 2014
Available online 3 January 2015

Keywords:
Thermal expansion
Heat capacity
Speed of sound
Density
Compressed liquid α,ω-dihaloalkanes
Volume fluctuations
Isothermal equation of state
Modeling thermal expansion

A B S T R A C T

During this research, we present an acoustic method used for determination of the thermal properties, such as the thermal expansivities and heat capacities from 293.15 K to 313.15 K of compressed liquid α,ω-dibromoalkanes. A designed in our lab experimental apparatus has been used to measure the speed of sound in liquid dibromoalkanes on five isotherms between 293 and 313 K and at pressures up to 100 MPa. The measurement technique is based on a traditional single-reflector pulse-echo method with a single piezoceramic transducer. The speed of sound data were combined with values of density and isobaric heat capacity along one isobar at atmospheric pressure to calculate the density, thermal expansivity and heat capacity over the whole temperature and pressure range by means of the acoustic numerical method. To explore the possibility of analytical description of the data, we propose the method based on the continuation of inverse reduced volume fluctuations into a single-phase region. The resulting expression contains two parameters characterizing the inverse volume fluctuations in the liquid and the isobaric heat capacity along the referent line and allows to predict the density and the isobaric heat capacity for the whole studied region with the accuracy, which does not exceed 0.1% and 1% correspondingly.

1. Introduction

Nowadays, the acoustic method based on accurate measurements of the speed of sound propagation in high pressure liquids is one of the standard methods for precise determination of thermophysical properties of compressed liquids [1–3]. There are essentially two experimental methods of determining the speed of sound in liquids at elevated pressure and within a wide range of temperature [3]: first methods based on the measurement of the time the acoustic pulse travels through a known distance in the liquid and second group of methods based on the measurement of the phase shift. We used in our work the pulse-echo-overlap method which belonging to the first group i.e. measurements of the time of flight of a short sound signal over a precisely known distance in the sample liquid.

The knowledge of thermophysical properties of liquids has a huge relevance in applied areas of research, and such data are often used in design process in many industrial applications. One of the most desirable thermophysical quantities are thermal expansivity α_p, and heat capacity C_p, and such results are frequently used in flow, heat transfer and mass transfer calculations in many chemical and industrial processes. Thermal expansion of fluids must be considered in engineering high pressure applications where changes in dimension or density due to temperature are expected. Particularly, in the development of a high pressure injection equipment, the knowledge of the values of isobaric thermal expansion as a function of both temperature and pressure play a fundamental role in the solving of the continuity and energy equation [4,5]. Isobaric thermal expansion of compressed liquids characterize how temperature and pressure affect density.

Research in thermal hydraulics requires the analysis of thermal wedges and lubricant pressure distribution between a rough and a smooth surface in relative motion, the knowledge of thermal expansion of a new generation gear lubricants oil under elevated pressure is extremely important [6]. For each technical importance liquid, values of thermal expansion are required to compute the isothermal compressibility from the adiabatic compressibility [7].

---

[*] Corresponding author.
E-mail address: miroslaw.chorazewski@us.edu.pl (M. Chorążewski).

http://dx.doi.org/10.1016/j.ijthermalsci.2014.11.028
1290-0729/© 2014 Elsevier Masson SAS. All rights reserved.

Moreover, the compressible liquid flow with heat transfer occurs in nuclear reactor applications and requires the analyses to include thermal expansion coefficient, heat capacity data and theirs relations [8]. In many engineering thermal processing of materials such as extrusion involving heat transfer, the knowledge of thermal expansion coefficient is essential particularly in the solving of non-isothermal free convective transport equations [9].

A knowledge of the thermophysical properties of liquid halogenoalkanes is of high interest on account of their wide usage in science and industrial processes. As a case study have been chosen 1,3-dibromopropane, 1,4-dibromobutane, 1,5-dibromopentane, and 1,6-dibromohexane. Bromoalkanes have many industrial applications [10–13], the most common use of 1,4-dibromobutane is in the polymerothermal syntheses of functional nanocomposites [14] and as a linker in the selective oxidation of alcohols in aqueous solutions [15].

1,4-dibromobutane is use in the production of 1-phenyl-1-cyano-cyclopentane, which is an important intermediate in the synthesis of drugs such as caramiphene and semisynthetic penicillin [16]. 1,3-dibromopropane, 1,4-dibromobutane and 1,6-dibromohexane have been used in the synthesis of ionic liquid precursors [17]. Another reactions with halogenated compounds can be found elsewhere [18]. 1,4-dibromobutane also has been used as a solvent to reactions under high pressure [19]. α,ω-Dibromoalkanes plays important role in cycloalkylations in supercritical ethane at temperature 70 °C and pressure 11.0 MPa under phase transfer catalysis conditions to synthesize many important intermediate in the synthesis of pharmaceuticals [20].

In spite of such widespread use, there are still gaps in the thermophysical properties for haloalkanes under high pressure.

To the authors' best knowledge, acoustic and derived thermophysical properties of 1,4-dibromobutane and 1,6-dibromohexane considered in this work are a novelty and have not been reported in the scientific literature.

As far as we know, there are no any previous direct or indirect measurements of thermal expansion coefficient of 1,4-dibromobutane and 1,6-dibromohexane at elevated pressure and temperature in the open literature. We have found only values for densities of similar homologous series of α,ω-dichloroalkanes: 1,2-dichloroethane, 1,4-dichlorobutane and 1,6-dichlorohexane measured in the range of temperature (288–318) K and pressure only up to 20 MPa [21].

For tested dibromoalkanes, the speeds of sound were measured as a function of pressure and temperature. These experimental data have been used for the calculation of the densities and isobaric thermal expansivities at high pressure. The measurements were made for pressures up to 100 MPa and temperatures ranging from (293.15–313.15) K. As an integral part of this work, the densities for 1,4-dibromobutane and 1,6-dibromohexane have been measured in the temperature range from (273.15–363.15) K under atmospheric pressure. Thermal expansion coefficient at elevated pressures of liquid halogenated alkanes was derived from the ultrasonic measurements [36–38]. Method based on the continuation of inverse reduced volume fluctuations into a single-phase region [41,42] has been used to modeling of thermal expansivity of pure α,ω-dibromoalkanes.

2. Experimental section

2.1. Chemicals

1,4-dibromobutane and 1,6-dibromohexane were purchased from Avocado with a specified mole-fraction purity 0.99 and 0.98, respectively. Both compounds were further purified by fractional distillation. Only the middle fractions were collected, resulting in a liquid sample with a purity of more than 99% (by GLC). The mass fraction of water as determined by the Karl-Fischer titration method was less than 4×10^{-5} for both investigated compounds. Additionally, investigated liquids were dried with molecular sieve (Lancaster, type 3A, beads) and stored in the dark glass flask placed in a desiccator. The samples were degassed in an ultrasonic cleaner just before each measurement.

2.2. Speed of sound measurements

In the present work the pulse-echo-overlap method described in details by Papadakis [22] and modified in our laboratory was applied [23,24]. The speeds of sound at the frequency of 2 MHz were measured under atmospheric and elevated pressures by the use of two measuring sets with measuring vessels of the same acoustic path and construction based on a single transmitting-receiving ceramic transducer and an acoustic mirror. Both apparatus operate on the principle of the pulse-echo-overlap method. Details of the apparatus and experimental procedure can be found elsewhere [23,24]. Both instruments were calibrated with doubly distilled water. The standard values of the speed of sound in water at atmospheric pressure were taken from the polynomial reported by Marczak [25], which was obtained by compilation of the most reliable literature data. The measurements uncertainty was estimated at ± 0.5 m s^{-1} at atmospheric pressure, while the precision was an order of magnitude better [26]. The standard values of the speed of sound in water at elevated pressures were taken from the Kell and Whalley polynomial [27]. The uncertainty of the measurements under elevated pressure was estimated to be better than ± 1 m s^{-1}. The pressure was measured using Hottinger Baldwin System P3MD with an uncertainty better than ±0.15%. The temperature was measured using an Ertco Hart 850 platinum resistance thermometer certified by NIST with an uncertainty of ±0.05 K and resolution of 0.001 K. During the measurements, the stability of ±0.01 K was maintained. More details of the high-pressure device and the methodology of the measurements the speed of sound in liquids under elevated pressure can be found in our previous papers [23,24]. The speeds of sound in 1,4-dibromobutane and 1,6-dibromohexane were measured from (292–313) K.

2.3. Density measurements

Experimental densities at atmospheric pressure were measured using an Anton Paar DMA 5000 digital vibrating tube with an uncertainty better than $\pm 5 \times 10^{-2}$ kg m^{-3} and repeatability better than $\pm 5 \times 10^{-3}$ kg m^{-3}. The instrument was calibrated with air and re-distilled, and degassed water. For 1,4-dibromobutane and 1,6-dibromohexane the densities at atmospheric pressure have been measured in the temperature range from (273.15–363.15) K. More experimental details can be found in our previous papers [28–31].

3. Results and calculations using the acoustic method

Densities of 1,4-dibromobutane and 1,6-dibromohexane obtained in this work at 298.15 K are given in Table 1. Measured

Table 1
Comparison of densities, ρ, tested liquids with literature data at $T = 298.15$ K.

	This work[a]	Literature
1,4-dibromobutane		
$\rho/(\text{kg m}^{-3})$	1817.43	1816.77 [32]; 1820.41 [33]; 1818.1 [34]; 1819.44 [35]
1,6-dibromohexane		
$\rho/(\text{kg m}^{-3})$	1598.42	1596.58 [33]; 1599.43 [32]; 1596.3 [34]; 1601.80 [35]

[a] Standard uncertainty $u(\rho) = 0.05$ kg m^{-3}, $u(T) = 0.01$ K.