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5. APPLICATION OF ACOUSTIC METHOD FOR DETERMINATION OF THERMODYNAMIC PROPERTIES OF LIQUIDS

In memoriam: Andrzej Żak (†2006), Marek Waciński (†2007), Stefan Ernst (†2014) and
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5.1. Introduction

Thermodynamic properties of liquids can be studied by many experimental techniques. One of the possibility is application of acoustic methods [1-3]. Generally, acoustic investigations are the source of interesting and useful information relevant to variance molecular processes as well as a liquid structure at various temperatures as well as both at atmospheric and high pressures. In our laboratory at the beginning, the acoustic studies have been done in cooperation with the researchers from the Faculty of Chemistry of the University of Wroclaw, Institute of Fundamental Technological Research of The Polish Academy of Sciences in Warsaw and Aviation Institute in Warsaw. From the early stage in our laboratory, the acoustic studies of liquids were accompanied by works related to the design and construction of ultrasonic equipment for measuring both the speed of sound and absorption of ultrasonic wave propagation in liquids. Metrology and the improvement of ultrasonic measurements are still within the scope of our interests. The speed of ultrasound wave is a particularly interesting property to study as it provides a way to determination of many thermodynamic properties of liquids. Although this is an indirect method, the results are one of the most reliable and accurate because the speed of sound can be measured very accurately [4-6].

In the middle of the eighties construction works in our laboratory were focused on equipment for speed of sound measurements in liquids under atmospheric pressure. Works

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were continued in the following years, modifying the sets and improving their reliability and uncertainty. Sing-around and pulse-echo-overlap sets developed in our laboratory [4, 7, 8] were used and are used not only by own research team but also by researchers from other centers in Poland and abroad. For example, sing-around sets (patent-protected solution [9]) were used for investigations of liquids in Department of Chemistry of University of Warsaw, Medical University of Lublin, University of Thessaloniki in Greece [10, 11], and Ben Gurion University in Israel [12, 13]. Parallel to the sing-around method, the sets for pulse-echo-overlap measurements were continuously developed and modified. Such set (OPE-4F) is one of the basic elements of our laboratory equipment. This type of set was delivered to Institute of Experimental Physics of the University of Gdańsk. In the nineties, the set for speed of sound measurements under high pressure was developed. The acquired practical experience and the ability to measure the phase velocity, determined the choice of the pulse-echo-overlap method for this purpose. At the beginning, the works were done in a close cooperation with Aviation Institute in Warsaw [14]. Later, the new modified sets were developed on its own [15, 16]. Thanks to mastering the technique of speed of sound measurements under high pressure, the research capabilities of the team have been significantly expanded. As a result, pressure testing has become one of the our most important research areas. It should be noted that the acoustic investigations of liquids under high pressure are rare until now.

From the beginning we were also interested in the second basic parameter related to the propagation of ultrasonic waves, i.e. the absorption of ultrasound. The ultrasound absorption is closely related to energy dissipation caused by different irreversible processes occurring in the liquid and, consequently, is a source of valuable information about kinetic and thermodynamic parameters of molecular processes. Excluding acousto-optic methods, in principle, two main groups of measurement methods can be distinguished, i.e., the cavity resonator methods and the pulse-modulated traveling wave methods. We were and are focused on the standard pulse method with a variable path length, i.e. method belonging to the abovementioned second group. The constructed measuring set has been modified over the years, among others, the available frequency range has been expanded from 10-80 MHz [17], via 10-250 MHz [18], to 5-300 MHz today [19]. This set type was delivered also for Department of Chemistry of the University of Wrocław [20].

5.2. Determination of thermodynamic properties of liquids from the speed of sound

5.2.1. Theoretical background

Both sing-around and pulse-echo-overlap methods show specific advantages and disadvantages [4]. The key difference between mentioned above methods is that the sing-around method gives only the group velocity c_g, while the pulse-echo-overlap method gives the phase velocity c_f . The group velocity is related to phase velocity as follows

$$c_g = c_f - \lambda \cdot \left(\frac{\mathrm{d}c_f}{\mathrm{d}\lambda} \right), \tag{1}$$

where λ denotes the wavelength and f denotes the frequency of ultrasonic wave. In other words, the phase velocity is frequency dependent and only under specific conditions, i.e. if $(\mathrm{d}c_f /\mathrm{d}\lambda) = 0$, $c_g = c_f$. It is very important because c_g measurements are generally much easier than measurements of c_f and in many cases there is a very good solution. However, it should be always remembered that correct measurements of speed of sound with sets that are intended for group velocity measurements can be obtained only for a non-dissipative liquids. In practice, such instrumentation is only appropriate for use in the case of liquids where the distinction between both velocities is not significant. In the case of dissipative liquids, or specific dissipative regions, serious errors can occur. Thus, the use of this type of instrument is limited in terms of the systems under acoustic research. Unfortunately, most of the commercial acoustic sets are developed for measurements in non-dissipative conditions because mostly wide-band technique is adopted. Thus, it should be emphasized once more that such instrumentation is not suitable for testing dissipative liquids. Moreover, thermodynamic properties can only be correctly determined acoustically when no relaxation processes are present, i.e. when “thermodynamic” speed of sound is determined, which can be used in so-called Newton-Laplace equation (or called the Laplace equation [21] or the Wood equation [1]). The fundamental relation between the speed of sound and thermodynamic properties is

$$c_f^2 = \left(\frac{\partial p}{\partial \rho} \right)_S, \tag{2}$$

where p is the pressure, ρ is the density and S is the entropy. This relation is exact in homogeneous non-dissipative liquid when isentropic approximation applies, i.e. in the limit of: (i) small amplitude and (ii) low frequency. In other words, the speed of sound of longitudinal wave is independent of amplitude, independent of frequency at the low frequency limit, λ is much smaller than the sample dimension and any scattering is present. From here, the c_f is denoted as c throughout this paper. The Eq.(2) presented above can be written in the form known as the Newton-Laplace equation

$$\kappa_S = \frac{1}{\rho \cdot c^2} . \tag{3}$$

This equation is a link between acoustic and thermodynamic formalism because it relates the speed of sound c which is a mechanical property with the isentropic compressibility κ_S which is a thermodynamic property.

5.2.2. Thermodynamic properties of liquids under atmospheric pressure

The κ_S can be obtained by relatively easy measurements of ρ and c. It should be noted that Eq.(3) is the only one way to obtain reliable κ_S values. Knowing κ_S, the isothermal compressibility κ_T can be determined from the well-known thermodynamic relation

$$\kappa_T = \kappa_S + \frac{\alpha_p^2 \cdot T \cdot V}{C_p}, \tag{4}$$

where V denotes molar volume, α_p denotes the isobaric thermal expansion, C_p is the molar isobaric heat capacity and T temperature. The κ_T and α_p are two fundamental thermoelastic material constants which are mainly reported in tables for characterization of materials. The third material constant is usually not reported because can be calculated from the simple relation between κ_T and α_p

$$\beta_V = \frac{\alpha_p}{\kappa_T}, \tag{5}$$

where β_V denotes pressure isochoric coefficient. In other words, only two thermoelastic material constants are independent.

The next determinable quantity is the isochoric heat capacity which is very difficult and tedious to determine directly. The molar isochoric heat capacity C_V can be determined from relation

$$C_V = C_p - \frac{\alpha_p^2 \cdot T \cdot V}{\kappa_T}. \tag{6}$$

In the next step, knowing C_V and C_p, the C_p/C_V ratio can be calculated.

Yet another interesting property is internal pressure P_{int}. The internal pressure can be calculated from relation

$$P_{\text{int}} = T \cdot \beta_V - p = T \cdot \frac{\alpha_p}{\kappa_T} - p. \tag{7}$$

At atmospheric pressure, the p term can be neglected without significant error because $p << T \cdot \alpha_p \cdot \kappa_T^{-1}$. However, at high pressures, this term must be taken into account. The internal pressure P_{int} is a next property that is presently obtained mainly via speed of sound measurement, i.e., by the indirect acoustic method (κ_T is calculated by Eq.(4)) and this method is one of the more convenient and well-established ways for determination of P_{int} [22, 23].

Note that sometimes it will be convenient to use molar quantities only. The molar counterparts of κ_S, κ_T and α_p, are $K_S = \kappa_S \cdot V$, $K_T = \kappa_T \cdot V$ and $E_p = \alpha_p \cdot V$, respectively. It is also worthy of note that according to the concept of Gibbsian and non-Gibbsian properties [24], K_T, E_p, and C_p as well as κ_T and α_p are Gibbsian properties, whereas K_S, E_S (molar isentropic thermal expansion), and C_V as well as κ_S, and α_S (isentropic thermal expansion) are non-Gibbsian properties. Nevertheless, the non-Gibbsian properties can be expressed in terms of Gibbsian properties [24].

Summing up, from simultaneous determination of $c(T)$, $\rho(T)$ and $C_p(T)$ various related thermodynamic quantities can be obtained. At atmospheric pressure, each of these three quantities can be experimentally determined over the wide temperature range with high or at least satisfactory accuracy, mostly by means of commercially available equipment, e.g. density and sound analyser as well as differential scanning calorimeter (reference [25] can be a good example). However, under high pressures, the case is much more complicated.

5.2.3. Thermodynamic properties of liquids under high pressure

As mentioned, under high pressures the problem is more complicated. For example, contrary to the $\rho(T)$ values, accurate and reliable experimental measurements of $\rho(T,p)$ are still one of the long-standing problems in experimental thermodynamics. Also, accurate prediction of that quantity is still an important and in practice unsolved problem. Generally, the lack of the $\rho(T,p)$ values or imperfect knowledge of the $\rho(T,p)$ values is of commercial/technological and scientific consequence. Also the accurate and reliable $C_p(p,T)$ data are very difficult to obtain experimentally, contrary to $C_p(T)$.

Direct measurements of properties such as density, heat capacity or compressibility are very difficult at high pressures. Since the speed of sound is closely linked with abovementioned properties and can be measured relatively easy with low uncertainty over wide ranges of p and T, therefore the acoustic method is very useful at high pressures. Using experimental pressure-temperature speed of sound data together with density and isobaric heat capacity data at reference pressure, mostly atmospheric pressure, the $\rho(p,T)$ and $c_p(p,T)$ data (c_p denotes specific isobaric heat capacity) can be obtained by proper integration procedures. However, for obtaining the $\rho(p,T)$ and $c_p(p,T)$ data, the speed-of-sound data must be firstly approximated and then integrated in the experimental (p,T) range. The efficient implicit cubic equation recommended by Sun et al. [26] is one of the best relations for description of the speed of sound surface on pressure and temperature

$$p - p_0 = \sum_{i=1}^{3} \sum_{j=0}^{1} a_{ij} \left(c - c_0\right)^i T^j , \tag{8}$$

where a_{ij} are the adjustable coefficients and c_0 denotes speed of sound at atmospheric pressure which is approximated by the polynomial in the form

$$c_0 = \sum_{j=0}^{2} b_j \cdot T^j , \tag{9}$$

where b_j are the adjustable coefficients.

In the calculations of $\rho(p,T)$ and $c_p(p,T)$ data, a modified numerical procedure [27] based on the earlier suggestions of Davies and Gordon [28] is mostly applied. A reference density and isobaric heat capacity as a function of temperature smoothed by polynomials in the same form as Eq.(9) at the atmospheric (reference) pressure are used.

The applied acoustic method is based on relationship between isothermal and isentropic compressibilities (Eq.(4)). Inserting into Eq.(4), the Newton-Laplace formula (Eq.(3)) and definition of isothermal compressibility $\kappa_T \equiv \rho^{-1} \cdot (\partial\rho/\partial p)_T$, leads to the following relationship

$$\left(\frac{\partial\rho}{\partial p}\right)_T = \frac{1}{c^2} + \frac{T\alpha_p^2}{c_p}, \tag{10}$$

and then by integrating the above equation (Eq.(10)), the formula describing change of density, $\Delta\rho$, caused by the change of pressure from p_1 to p_2 at constant temperature is obtained

$$\Delta\rho = \int_{p_1}^{p_2}\left(\frac{1}{c^2} + \frac{\alpha_p^2 T}{c_p}\right)\mathrm{d}p \approx \int_{p_1}^{p_2}\frac{1}{c^2}\mathrm{d}p + \frac{\alpha_p^2 T}{c_p}\Delta p, \tag{11}$$

where $\Delta p = p_2 - p_1$. The approximate relationship (Eq.(11)) is sufficiently accurate, provided that Δp is small, because the isobaric heat capacity depends only slightly on pressure. The first integral on the right-hand side can be obtained directly, whereas for the second integral, an appropriate integration procedure must be used. Note also that the first integral is significantly larger than the second one, since the latter term results from the difference between the isentropic and isothermal compressibilities, which is rather small. The specific isobaric heat capacity at p_2 is given by

$$c_p(p_2) \approx c_p(p_1) - (T/\rho)\{\alpha_p^2 + (\partial\alpha_p/\partial T)_p\}\Delta p, \tag{12}$$

where $c_p(p_1)$ is the specific isobaric heat capacity at p_1.

The respective uncertainties estimated by means of the perturbation method [29, 30] (the speed of sound is taken into account as a main source of the uncertainty) are expected to be better than ±0.3% and ±0.02% for the isobaric heat capacity and density, respectively [31-34]. However, as reported previously [33, 35], the total uncertainties (including a comparison of most results obtained in our laboratory with those obtained in other laboratories by different methods) can be estimated roughly to be better than ±1% and ±0.05% for the heat capacity and density, respectively. From the consistent data sets of $c(p,T)$, $\rho(p,T)$ and $c_p(p,T)$ all related thermodynamic properties such as $\kappa_S(p,T)$, $\kappa_T(p,T)$, $\alpha_p(p,T)$, $C_V(p,T)$, $P_{\mathrm{int}}(p,T)$ can be obtained by using the Newton-Laplace relation and standard thermodynamic relations. Simultaneously, because c can be measured with very low uncertainty over the wide range of p and T, the possibility of $\rho(p,T)$ determination from $c^{-2}(p,T)$ is a very attractive one (see Eq.(10)) in comparison to other experimental techniques such as: piezometers, dilatometers, high-pressure vibrating-tube densimeters, or high-pressure calorimeters. We showed that the speed of sound and isentropic compressibility obtained by densimetric method are not in a good agreement with the results determined by the acoustic one [6, 36, 37].

5.3. Investigations of acoustic and thermodynamic properties of liquids at atmospheric pressure

5.3.1. Molecular liquids and ionic liquids

Investigations of the speed of sound and thermophysical properties of pure molecular liquids such as for example alkanes, alcohols, and esters of fatty acids together with ionic liquids (ILs) allowed to find exciting properties such as high isobaric heat capacity, low isentropic and isothermal compressibility of ILs and the subtle effects of alkyl chain length of ILs especially on the speed of sound in ILs. The high isobaric heat capacity, low isentropic and isothermal compressibility of ILs (see Fig. 1) together with their high thermal stability and non-flammability predestined them as attractive potential heat transfer fluids [38, 39] and hydraulic fluids [40]. The emergence, growing availability and promising properties of ILs as well as rapidly growing interest in them have also directed our interest in this direction during last two decades. As known, ILs are substances usually composed of a large organic cation with a low degree of symmetry, and an organic or inorganic anion, that have much lower melting points (below 373 K) in relation to the conventional molten salts. Although ILs are very interesting and promising substances both for academia and industry and they have been extensively studied, their properties are not known enough. This also applies to the acoustic and thermodynamic properties. During last years in a series of articles the consistent thermodynamic data sets for various types of ILs were reported. One of the interesting properties is compressibility because ILs can be potentially good working fluids. For all ILs studied, both κ_S and κ_T increase with temperature at atmospheric pressure. The values of κ_S and κ_T increase also with the increasing alkyl chain length, *n*, in the cation in the homologous series contrary to for example 1-alkanols and methyl esters (see Fig. 1). In other words, the lower member of the homologue series shows enhanced structural rigidity in comparison to the higher member [25, 41]. The speed of sound in ILs with smaller anions such as tiocyanate $[SCN]^-$, tetrafluoroborate $[BF_4]^-$, hexafluorophosfate $[PF_6]^-$ decreases with alkyl chain length in cation. For ILs with bis(trifluoromethylsulfonyl)imide anion $[NTf_2]^-$, the minimum of the speed of sound dependence on alkyl chain length in cation $u(n)$ is observed, i.e. for 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides $[C_nC_1im]$ $[NTf_2]$ [25, 41, 42], N-alkylpyridinium bis(trifluoromethylsulfonyl)imides $[C_npy][NTf_2]$ [43] (see Fig. 1) as well as pyrrolidinium-based bis(trifluoromethylsulfonyl)imides [44]. While for the homologous series of imidazolium-based ILs with a trifluoromethylsulfonate anion $[C_nC_1im][TFO]$ [44] the intermediate dependence $c(n)$, between approximately linear for ILs with smaller anions (eg.

$[SCN]^-$, $[BF_4]^-$, $[PF_6]^-$) and the minimum of *c*(*n*) dependence for ILs with $[NTf_2]^-$ anion, was found [44]. In turn, in case of molecular solvents such as 1-alkanols [37, 45-49] and methyl esters [50], nonlinear increase of the speed of sound is observed (see Fig. 1).

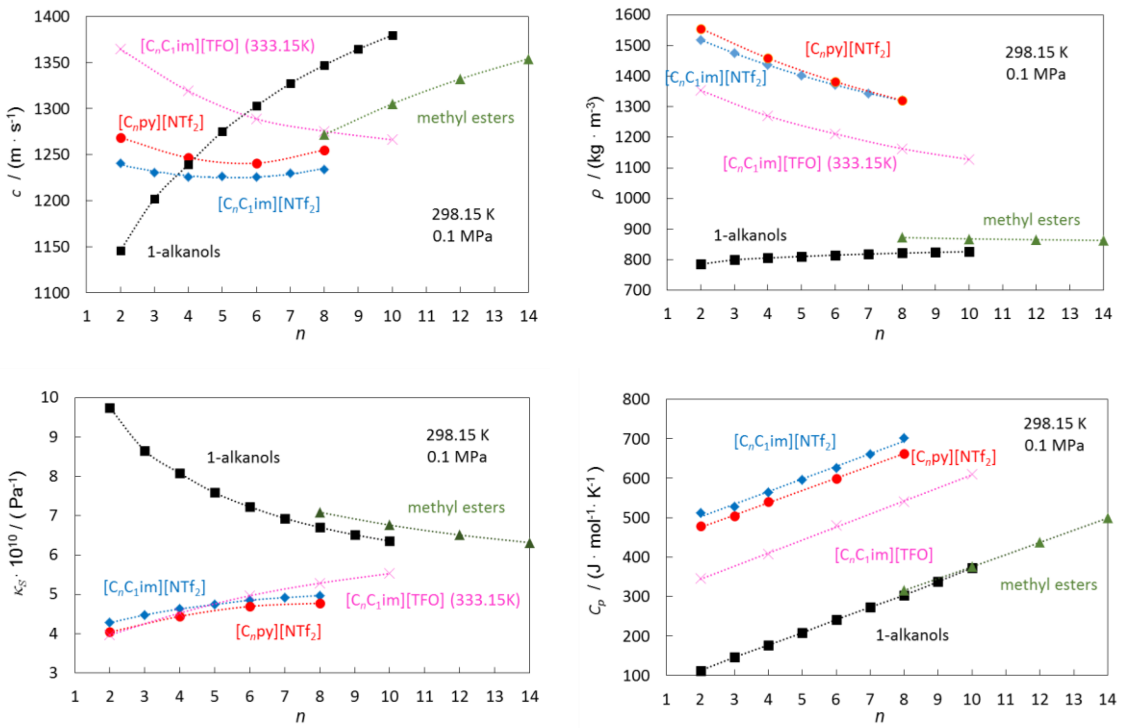

Fig. 1. The effect of alkyl chain length (*n*) on speed of sound (*c*), density (ρ), isentropic compressibility (κ_S), molar isobaric heat capacity (C_p) of 1-alkanols [37,45-52], methyl esters [53], 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides $[C_nC_1im][NTf_2]$ [25,41,42], N-alkylpyridinium bis(trifluoromethylsulfonyl)imides $[C_npy][NTf_2]$ [43], 1-alkyl-3-methylimidazolium trifluoromethanesulfonates $[C_nC_1im][TFO]$ [44] at atmospheric pressure and at temperature 298.15 K

Rys. 1. Wpływ długości łańcucha alkilowego (*n*) na prędkość (*c*), gęstość (ρ), ściśliwość izoentropową (κ_S), molową izobaryczną pojemność cieplną (C_p) 1-alkanoli [37,45-52], estrów metylowych [53], bis(trifluorometylosulfonylo)imidów 1-etylo-3-metyloimidazoliowych $[C_nC_1im][NTf_2]$ [25,41,42], bis(trifluorometylosulfonylo)imidów N-alkilopirydyniowych $[C_npy][NTf_2]$ [43], trifluorometanosulfonianu 1-etylo-3-metyloimidazoliowego $[C_nC_1im][TFO]$ [44] pod ciśnieniem atmosferycznym i w temperaturze 298.15 K

The minimum of *c*(*n*) dependence for ILs with the $[NTf_2]^-$ anion in the range of $n = 4÷6$ at atmospheric pressure can confirm segregation of polar and nonpolar domains from globular into sponge-like structure with increasing alkyl chain length in the cation.

5.3.2. Solutions of electrolytes, viscous polyhydroxyalcohols, and aqueous solutions of picolines

In the early stage, the research was aimed to compressional and shear processes in solutions of electrolytes in polyhydroxyalcohols [54, 55], at applications of acoustic methods for study of molecular parameters [56], and for ultrasonic and rheological properties of viscous polyols as well as their mixtures [57-59]. Among others, the importance of hydrogen bondings in determining the shear elasticity of polyhydroxyalcohols and their mixtures was shown [57]. It was also found that positional and orientational correlations as well as gearing effect contribute to the broad distribution of viscoelastic relaxation times [58, 59].

In a certain period, aqueous solutions were the subject of research by part of the team. The subjects of experimental and model studies carried out in the nineties were thermodynamic properties of aqueous solutions of electrolytes [60-62]. In the nineties and in the first decade of the XXIst century, the hydrophobic and hydrophilic hydratation phenomena of picolines in aqueous solutions were intensively studied as well [63-67].

5.3.3. Molecular liquids and their binary mixtures

However, the binary systems of molecular liquids such as alcohol + alcohol, alcohol + cycloalkane, alcohol + alkane, dichloroalkane + alkane, and alkane + alkane were the key area of research during the many years [57, 68-73].

The acoustic and thermodynamic properties of alcohol + alcohol mixtures were investigated almost from the beginning of our research team [57]. There are very interesting but simultaneously very difficult systems because both components are polar and self-associated. In consequence, in such systems various types of interactions are present and the separation of these effects is extremely difficult and practically the problem has not been finally resolved until today.

Very interesting is the examination of the effect of the placement of hydroxyl groups in the isomeric alkanediols on the physicochemical properties. The results reported for isomeric butanediols (1,2-, 1,3-, and 1,4-) in systems with 1-butanol [69] show that the system with 1,2-butanediol exhibits the smallest excess molar compressibility, molar volumes and speed of sound deviations. On the other hand, the system with 1,4-butanediol shows the greatest excesses. Thus, the results indicate that position of the hydroxyl groups in butanediol molecules has an effect on the molecular interactions and local structures. In turn, in the case of binary systems of 1,2-ethanediol with 1-alkanols the clear dependence on carbon alkyl chain in 1-alkanol molecules is visible [74]. For example, the excess molar isentropic compressibility K_S^E decreases at 298.15 K in the order: 1-nonanol >1-octanol >1-heptanol > 1-hexanol >1-pentanol >1-butanol >ethanol >methanol. However, up to 1-heptanol, K_S^E is negative over the whole concentration range, whereas for 1-octanol and 1-nonanol K_S^E is S-shaped. This is due to structural changes of the systems caused by the participation of the two alcohols in the dynamic intermolecular association process through hydrogen bonding.

The acoustic and thermodynamic properties of alcohol + alkane and alkane + alkane mixtures as a function of temperature under atmospheric pressure were investigated in order to obtain data at reference conditions, i.e. temperature dependence under ambient pressure, for the high pressure study. Therefore, the detailed description of the properties of these binary systems is presented in the next section (see section 5.4.2).

5.4. Investigations of acoustic and thermodynamic properties of liquids under high pressures

5.4.1. Molecular liquids and ionic liquids

The first thermodynamic properties under high pressures obtained in our team were reported for 1-alkanols. The subject of the research was 1-alkanols from ethanol to 1-decanol [37, 45-49]. The isomers of pentanol such as 2-methyl-1-butanol, 2-methyl-2-butanol and cyclopentanol, which differ in the position of the hydroxyl group in the carbon chain and in the structure of the carbon chain were also investigated. Thus, they are characterized by a different ability to form hydrogen bonds as well as the type of associates [48, 75-77].

In a modern common rail fuel injection system in diesel engines, the pressure reaches a maximum of 300 MPa, and the injection process is approximately adiabatic. Therefore, it is not surprising that adiabatic compressibility is particularly useful for the optimization of the common rail engines. Fuel density also affects the mass of fuel injected into the combustion chamber and in consequence, the fuel-air ratio. The efficiency of the combustion process and the toxicity of the exhaust gases depend on the physicochemical properties of the fuel. The density, isentropic compressibility, isobaric thermal expansion and isobaric heat capacity are among the most important properties for characterizing the quality of fuels. Therefore, according to constructed in our laboratory high pressure device, the systematic study of the biodiesel produced in Poland by Refinery Trzebinia [78], and components of I and II generation biofuels such as methyl esters [53], ethyl esters [79], 2-methylfuran and 2,5-dimethylfuran [80] were conducted. The obtained results showed that differences of properties of fuel components, especially differences of density and isentropic compressibility, can be compensated by temperature and/or pressure. Moreover, some subtle structure effects were observed. The density of fatty acid methyl esters is greater than the density of their ethyl counterparts. This difference is greater than that of an additional methylene group in the ethyl ester molecule. This is the effect of changing a certain order of molecules in the liquid, similarly to the crystalline phase, as stated for methyl and ethyl stearate. In the unit cell of the methyl stearate crystal there are eight molecules while the ethyl stearate has four molecules. In turn, in the groups of methyl or ethyl esters of fatty acids, the density decreases with the increase of alkyl chain length of a fatty acid at lower temperatures and above the temperature characteristic for each group of methyl and ethyl esters, the density increases with the increase of alkyl chain length of a fatty acid. The temperature of the inversion is higher for methyl esters than for ethyl esters. Observed inversion temperatures for methyl [53] and ethyl esters [79] are higher than achievable at high pressure investigations carried out in our laboratory. Extrapolation of $p\rho T$ data obtained by the acoustic method to higher temperatures indicated that this effect probably exists under high pressure.

The ILs are characterized by a variety of properties resulting from variety of structure of cations and anions. Seemingly small changes in the structure of ILs could lead to significant changes in intermolecular interactions, and consequently to change in the properties of ILs. The inspiration to undertake the systematic high pressure acoustic investigations of ILs was the fact that 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[C_6C_1im][NTf_2]$ was as the IUPAC standard indicated for speed of sound at atmospheric pressure and high pressure density, and it was not indicated for speed of sound under high pressures [5]. The results of ultrasound absorption under atmospheric pressure, which have been obtained up to now suggest that decreasing temperature and/or increasing pressure shift the relaxation region towards lower frequencies for aprotic ILs, similarly as for strongly associated molecular liquids [5]. The values of the classic absorption coefficient, α_{class}, can be estimated by Stokes formula using speed of sound, density and viscosity. This allows to determine temperature and pressure for which the dissipative processes are neglected for aprotic ILs as follows: $2\cdot \alpha_{\text{class}}\cdot c_0\cdot (2\cdot\pi\cdot f)^{-1} << 1$ [5] and to choose the appropriate method of measurement (group or phase velocity), and consequently to obtain the thermodynamic speed of sound. The proposed method is the only one that makes it possible to estimate the ultrasound absorption for ILs under high pressure because high-pressure ultrasound absorption for ILs has never been measured yet. If the specified above experimental conditions are fulfilled, the acoustic method, although it is an indirect one, allows to obtain the most reliable thermodynamic data for the compressed liquids [6]. The effect of alkyl chain length on speed of sound, density, isentropic compressibility, and molar isobaric heat capacity of 1-alkanols [37, 45-49], methyl esters [53], $[C_nC_1im][NTf_2]$ [36, 81], $[C_npy][NTf_2]$ [82] at 100 MPa and at 298.15 K is presented in Fig. 2. For molecular liquids the similar trends as under ambient pressure are observed, while for ILs with $[NTf_2]^-$ anion, with the increasing pressure the minimum of $c(n)$ dependence moves towards IL with a shorter alkyl chain in the cation (compare Fig. 1 and Fig. 2).

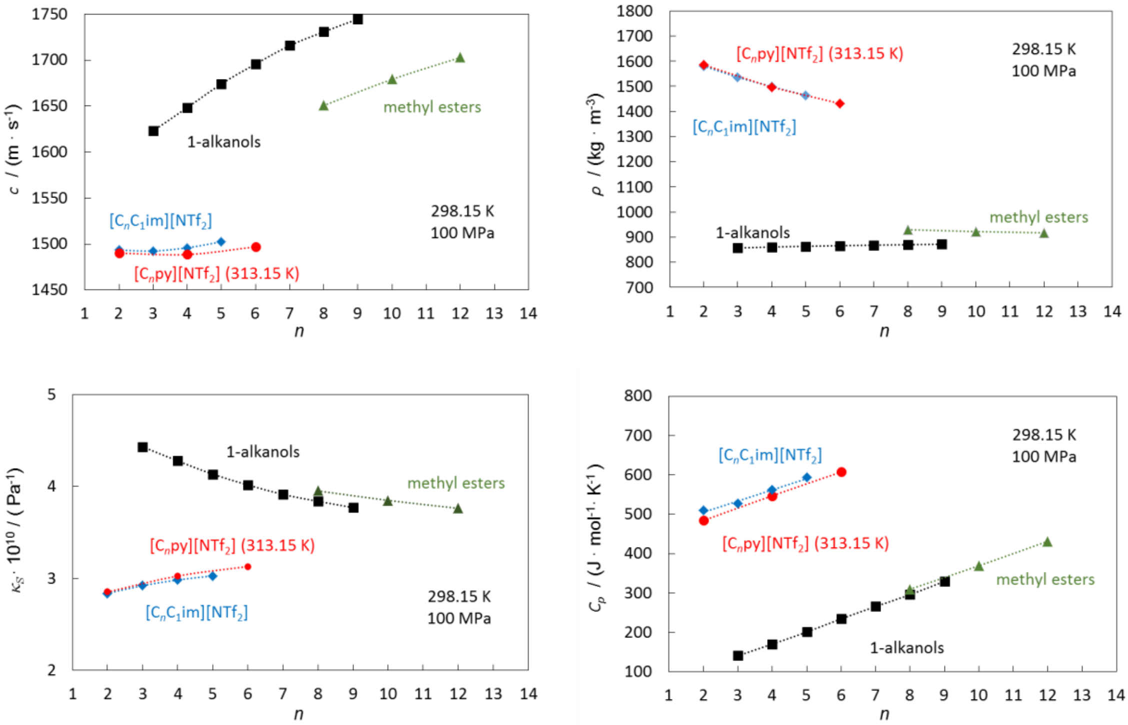

Fig. 2. The effect of alkyl chain length (*n*) on speed of sound (*c*), density (*ρ*), isentropic compressibility (κ_S), molar isobaric heat capacity (C_p) of 1-alkanols [37, 45-49], methyl esters [53], 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides [$C_nC_1$im][NTF_2] [36, 81], N-alkylpyridinium bis(trifluoromethylsulfonyl)imides [$C_n$py][NTF_2] [82] at pressure 100 MPa and at temperaturę 298.15 K

Rys. 2. Wpływ długości łańcucha alkilowego (*n*) na prędkość ultradźwięków (*c*), gęstość (*ρ*), ściśliwość izoentropową (κ_S,) i molową izobaryczną pojemność cieplną (C_p) 1-alkanoli [37, 45-49], estrów metylowych [53], bis(trifluorometylosulfonylo)imidów 1-etylo-3-metyloimidazoliowych [$C_nC_1$im][NTF_2] [36, 81], bis(trifluorometylosulfonylo)imidów N-alkilopirydyniowych [$C_n$py][NTF_2] [82] pod ciśnieniem 100 MPa i w temperaturze 298.15 K

Very interesting results are obtained for lower alkanediols. It appears that clear differences in the behavior of lower linear 1,2-diols and α,ω-diols are observed [83]. It is indicated in Fig. 3 that the effect of elongation of the carbon chain length in α,ω-, and 1,2-diols is different. In the case of 1,2-diols, K_S increases more rapidly than in the case of α,ω-diols. Thus, the results show that the $-CH_2$ group contribution to K_S is clearly higher for isomers with two adjacent hydroxyl groups (1,2-), whereas the increase of carbon chain length with a simultaneous increase in the distance between the hydroxyl groups (α,ω-) leads to the smaller $-CH_2$ group contribution. Similar linear relations are also observed in the case of K_T (Fig. 3).

Very high compressibility, the highest of all the diols under consideration, is observed in the case of 2-methyl-2,4-pentanediol due to its branching carbon chain. Thus, the existence of the side methyl group strongly affects the compressibility (twice or more) in comparison with the linear alkanediols [83]. In point of fact, the difference is visible for all properties studied. First and foremost, it is due to the difference in the molecular structure: 2-methyl-2,4-pentanediol has a branched carbon chain and is a relatively unsymmetrical molecule with terminal non-polar parts (three CH_3 groups), whereas all the rest of the alkanediols have a linear carbon chain.

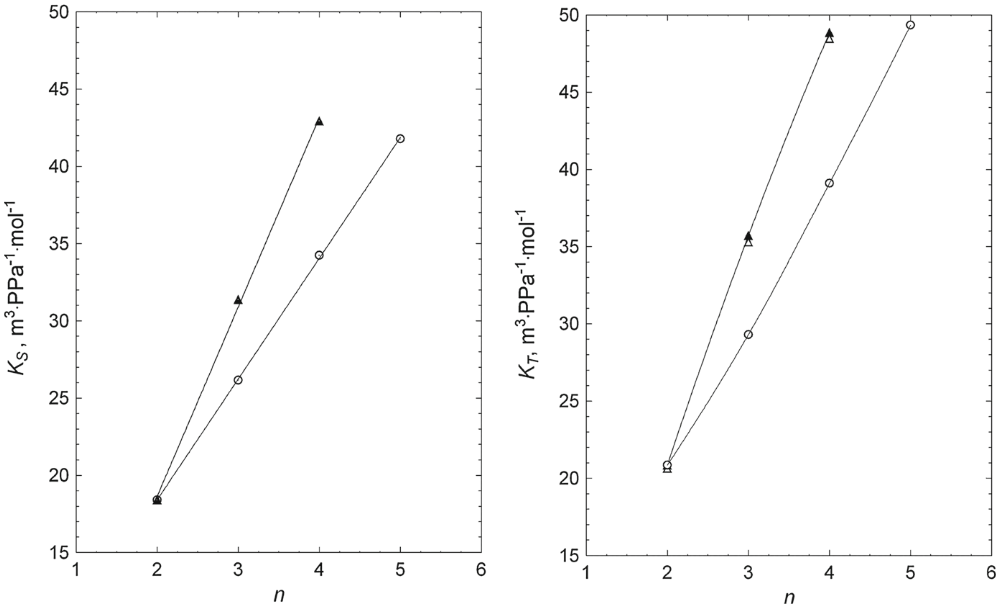

Fig. 3. Molar isentropic (K_S) and molar isothermal (K_T) compressibility plotted against number of carbon atoms (n) in alkanediol molecule at pressure 0.1 MPa and at temperature 298.15 K for: (▲, Δ), 1,2-alkanediols; and (○), α,ω-alkanediols. Straight lines – obtained by fitting of the K_S and K_T values. Reproduced from Int. J. Thermophys. 35 (2014) 890–913 ([83]) Copyright 2014 Springer Nature

Rys. 3. Molowa ściśliwość izoentropowa (K_S) i izotermiczna (K_T) w funkcji liczby atomów węgla (n) w cząsteczce alkanodiolu pod ciśnieniem 0.1 MPa i w temperaturze 298.15 K dla: (▲, Δ), 1,2-alkanodioli; i (○), α,ω-alkanodioli. Linie – uzyskane przez dopasowanie wartości K_S and K_T. Zreprodukowane z Int. J. Thermophys. 35 (2014) 890–913 ([83]) Copyright 2014 Springer Nature

It is known that the pressure-temperature behavior of the isobaric thermal expansion of liquids can be analyzed as a macroscopic manifestation of the effects existing at molecular level. For molecular liquids isobaric thermal expansion increases with increasing temperature at constant pressure up to the crossing point (see Fig. 4) and then it decreases. The pressures of crossing points of isobaric thermal expansion isotherms of alkanes and esters are lower than 100 MPa. For associated liquids a shift of the crossing points toward the higher pressure region is observed; for example, for 1-hexanol the crossing point is at ca. 280 MPa, while for water is observed at about 450 MPa [84]. Moreover, this specific behavior of isobaric thermal expansion was also observed for more complicated systems such as petroleum diesel oil and biodiesel fuel [78]. According to strong coulombic interactions in ILs, the temperature dependence of the isobaric thermal expansion under atmospheric pressure is weak. For some ILs isobaric thermal expansion decreases with increasing temperature under atmospheric pressure as in case of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C_2C_1im][NTf_2] [81], 1-ethyl-3-methylimidazolium ethyl sulfate [C_2C_1im][$EtSO_4$] [40]. For these two ILs at high pressure the isobaric thermal expansion decrease with temperature becomes slightly stronger (see Fig. 4).

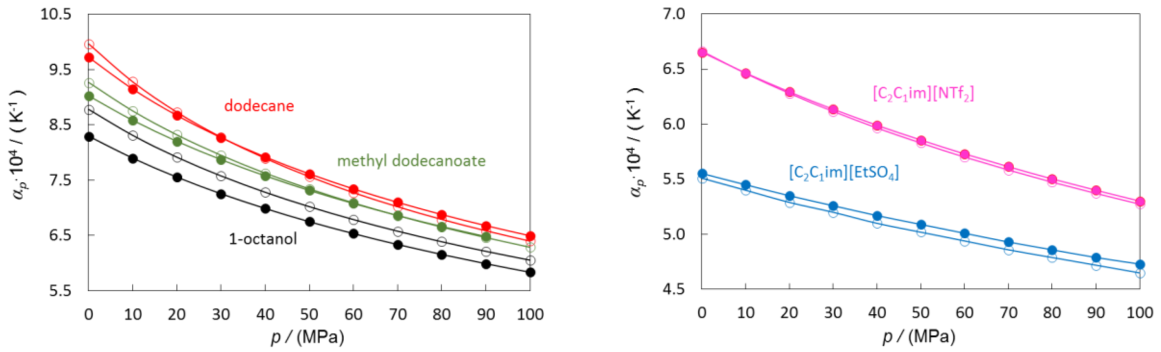

Fig. 4. The effect of pressure (p) on isobaric thermal expansion (α_p) of dodecane [88], methyl dodecanoate [53], 1-octanol [49], 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide [C_2C_1im][NTf_2] (calculated from [81]), 1-ethyl-3-methylimidazolium ethyl sulfate [C_2C_1im][$EtSO_4$] [40] at temperature 293.15 K (full symbols) and 318.15 K (empty symbols)

Rys. 4. Wpływ ciśnienia (p) na izobaryczną rozszerzalność termiczną (α_p) dodekanu [88], dodekanianu metylu [53], 1-oktanolu [49], bis(trifluorometylosulfonylo)imidu 1-etylo-3-metyloimidazoliowego [C_2C_1im][NTf_2] (obliczone z [81]), siarczanu etylu 1-etylo-3-metyloimidazoliowego [C_2C_1im][$EtSO_4$] [40] w temperaturze 293.15 K (pełne symbole) i 318.15 K (puste symbole)

Using acoustic method, P_{int} was determined for such molecular organic liquids as: alkanes, alkanols, alkanediols and esters, as well as various ILs. Inspection of the results shows that except of alkanediols, P_{int} at atmospheric pressure decreases with increasing temperature (the $(\partial P_{int}/\partial T)_p$ values are negative) for both molecular liquids and ILs under investigations (Fig. 5). Thus, the negative $(\partial P_{int}/\partial T)_p$ values are typical both for molecular organic liquids and ILs. Exceptions are the substances that form a spatial network of hydrogen bonds where the positive $(\partial P_{int}/\partial T)_p$ values occur. This type of behavior concerns for example some polyols [32, 34] and water [85]. The pressure dependence of P_{int} is more complicated (Fig. 5). In most cases an extremum is observed. A detailed discussion about relation between temperature-pressure dependence of P_{int} and intermolecular interactions in ILs and molecular organic liquids was published recently [86]. The obtained results show that the temperature-pressure dependence of internal pressure depends on the structure of the molecular liquids and ILs and the nature of intermolecular interactions [86].

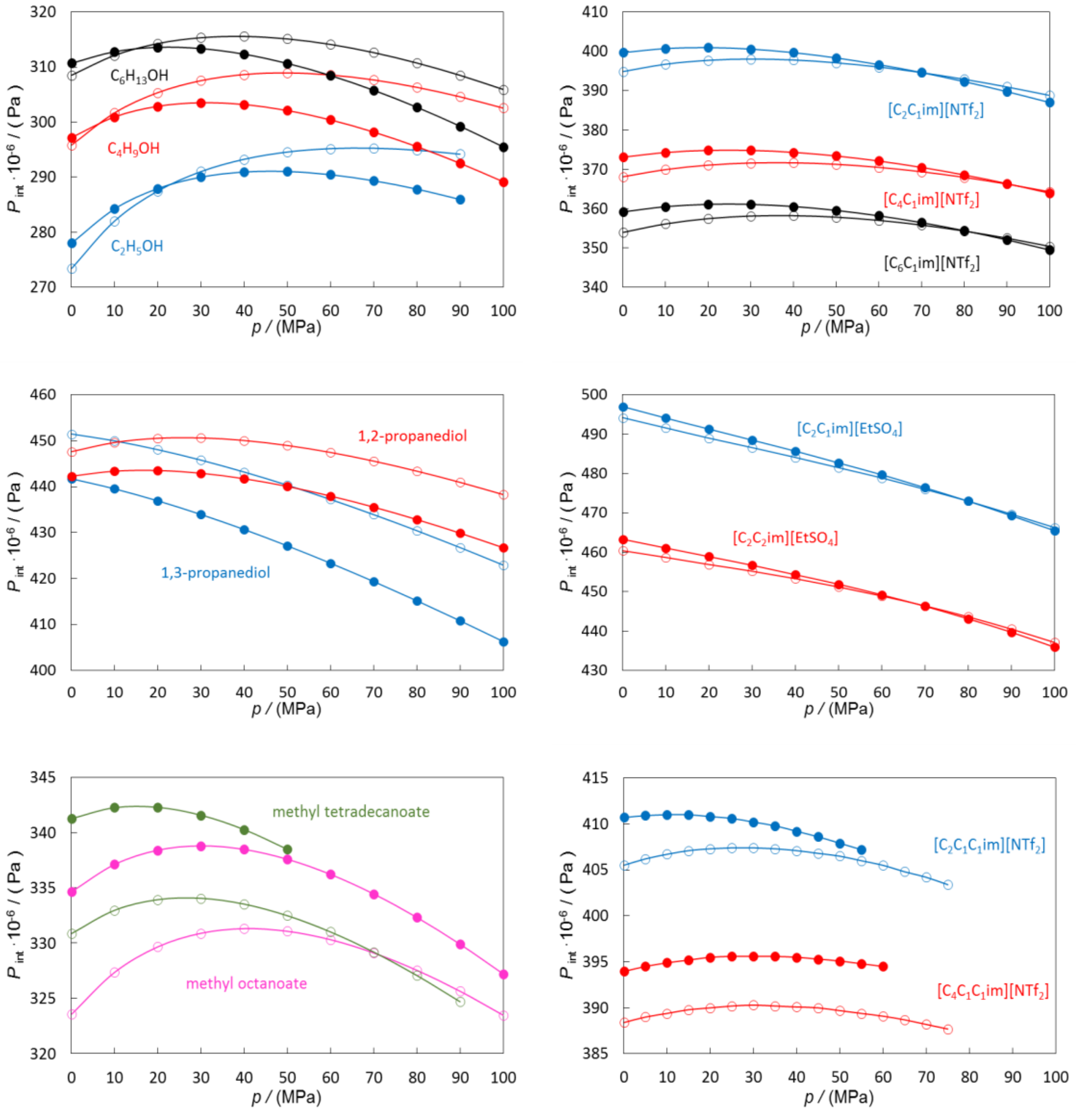

Fig. 5. The effect of pressure (*p*) on internal pressure (P_{int}) of ethanol C_2H_5OH [45], 1-butanol C_4H_9OH [37], 1-hexanol $C_6H_{13}OH$ [49], 1,2- and 1,3-propanediol [32], methyl dodecanoate and tetradecanoate [53], 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[C_2C_1im][NTf_2]$ [87], 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[C_4C_1im][NTf_2]$, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[C_6C_1im][NTf_2]$, 1-ethyl-3-methylimidazolium ethyl sulfate $[C_2C_1im][EtSO_4]$, 1,3-diethyl-imidazolium ethyl sulfate $[C_2C_2im][EtSO_4]$, 1-ethyl-2,3-dimethylimidazolium bis(trifluoro-methylsulfonyl)imide $[C_2C_1C_1im][NTf_2]$ and 1-butyl-2,3-dimethyl imidazolium bis(trifluoro-methylsulfonyl)imide $[C_4C_1C_1im][NTf_2]$ [86] at 303.15 K (full symbols) and 318.15 K (empty symbols)

Rys. 5. Wpływ ciśnienia (*p*) na ciśnienie wewnętrzne (P_{int}) etanolu C_2H_5OH [45], 1-butanolu C_4H_9OH [37], 1-heksanolu $C_6H_{13}OH$ [49], 1,2- i 1,3-propanodiolu [32], dodekanianu i tetradekanianu metylu [53], bis(trifluorometylosulfonylo)imidu 1-etylo-3-metyloimidazoliowego $[C_2C_1im][NTf_2]$ [87], bis(trifluorometylosulfonylo)imidu 1-butylo-3-metyloimidazoliowego $[C_4C_1im][NTf_2]$, bis(trifluorometylosulfonylo)imidu 1-heksylo-3-metyloimidazoliowego $[C_6C_1im][NTf_2]$, siarczanu etylu 1-etylo-3-metyloimidazoliowego $[C_2C_1im][EtSO_4]$, siarczanu etylu 1,3-dietyloimidazoliowego $[C_2C_2im][EtSO_4]$, bis(trifluorometylosulfonylo) imidu 1-etylo-2,3-dimetyloimidazoliowego $[C_2C_1C_1im][NTf_2]$ i 1-butylo-2,3-dimetyloimidazoliowego $[C_4C_1C_1im][NTf_2]$ [86] dla 303.15 K (pełne symbole) i 318.15 K (puste symbole)

5.4.2. Binary mixtures

The internal coherence of the measured speed of sound as a function of composition (mole fraction x_i), temperature and pressure together with density and isobaric heat capacity as a function of composition and temperature under atmospheric pressure is very important for determination of the relationship between density, temperature and pressure ($p\rho T$) and related quantities for mixtures [35, 88]. The internal coherence of the obtained ρ (x_i,p,T) and C_p (x_i,p,T) data allowed to determine the excess molar volume ($V^{\mathrm{E}} = V - x_1V_1^{\mathrm{o}} - x_2V_2^{\mathrm{o}}$, where V is the molar volume of mixture, V_i^{o} is the molar volume of pure i-component) and excess molar isobaric heat capacity ($C_p^{\mathrm{E}} = C_p - x_1C_{p,1}^{\mathrm{o}} - x_2C_{p,2}^{\mathrm{o}}$, where C_p is the molar isobaric heat capacity of mixture, $C_{p,i}^{\mathrm{o}}$ is the molar isobaric heat capacity of pure i-component), respectively, which was often connected with the observation of very subtle effects. To study the effect of alcohol structure on deviations from the ideal properties of binary mixtures with heptane, the binary mixtures of ethanol + heptane [45, 90], 1-decanol + heptane [50, 89] and 2-methyl-2-butanol + heptane [91, 92] were chosen. As a reference system, the mixtures of dodecane + heptane were investigated [88]. Already, the pressure dependence of the speeds of sound shows similarities and dissimilarities of investigated mixtures (Fig. 6). For ethanol + heptane mixtures the speed of sound in pure heptane (and mixtures rich in heptane) increases with increasing pressure more rapidly than in pure ethanol over the whole pressure range under investigation Finally speed of sound in pure heptane became higher than in ethanol (and mixtures rich in ethanol) at 90 MPa. Comparison of speed of sound in ethanol + heptane mixtures and in 2-methyl-2-butanol + heptane ones shows that the difference between speed of sound in pure 2-methyl-2-butanol and in mixtures rich in 2-methyl-2-butanol and in appropriate ethanol + heptane ones increases with increasing pressure. While in case of 1-decanol + heptane mixtures at pressures close to the atmospheric one, the speed of sound in heptane (and mixtures rich in heptane) depends more significantly on pressure than those in 1-decanol (and mixtures rich in 1-decanol). But with increasing pressure this effect decreases gradually and becomes comparable for all mixtures. Similar dependence was observed for dodecane + heptane mixtures [88] (in Fig. 6, c is plotted against the mole fraction of dodecane).

The volume effects on mixing of alcohol with alkane arise from the competition between two opposite contributions. The positive contribution involves the rupture of both dispersive and hydrogen bond interactions during mixing. The other one, namely packing contribution (connected with structure) – is negative and it comes from the fitting of the alkane molecules into the cavities or holes in the hydrogen-bonded structure of the alcohol.

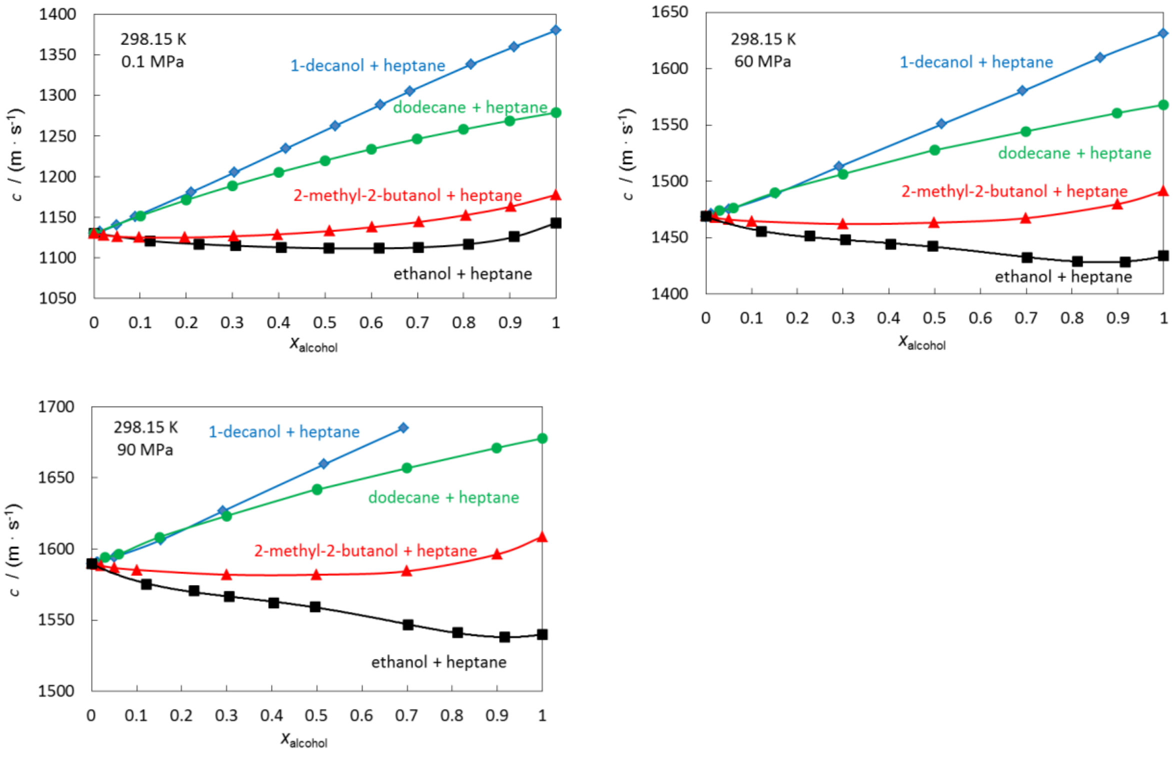

Fig. 6. The effect of pressure on concentration dependence of the speed of sound (*c*) in: ethanol + heptane [90], 2-methyl-2-butanol + heptane [91], dodecane + heptane [88], and 1-decanol + heptane [89]; *x* denotes mole fraction. Lines – arbitrary

Rys. 6. Wpływ ciśnienia na stężeniową zależność prędkości ultradźwięków (*c*) dla: etanol+heptan [90], 2-metylo-2-butanol+heptan [91], dodekan+heptan [88] i 1-dekanol+heptan [89]; *x* oznacza ułamek molowy. Linie – arbitralnie

The pressure dependence of excess molar volume of 1-decanol + heptane mixtures shows some similarities to that of dodecane + heptane (Fig. 7) in contrast to excess molar enthalpy and excess molar heat capacity for which pressure and temperature dependencies are opposite [88]. The excess volumes of dodecane + heptane mixtures are negative over the whole concentration range under atmospheric pressure and the deviations from the ideality increase with increasing temperature. This dependence is similar to that of 1-decanol + heptane in the region from the crossing point to high concentration of 1-decanol. It is commonly assumed that the negative volume deviations result mainly from the fitting of the shorter alkane molecules into the structure of the longer-chain alkanes. This leads to a more compact and less compressible structure. The volume effect of mixing decreases with increasing pressure, and at 293.15 K and under 50 MPa, the excess volumes become positive for mixtures rich in heptane. As it is known for alcohol + alkane mixtures positive volume effect of mixing is connected with disruption of hydrogen bonds. It seems that in case of dodecane + heptane mixtures, the positive volume effect of mixing is probably connected with rupture of the orientational order, i. e. weak association between dodecane molecules. It is interesting that the positive volume effect of mixing appears under high pressure. Thus, at higher pressures the repulsive forces cause an unrolling of the bended chains of dodecane. The interstitial accommodation of dodecane molecules into compact structure of heptane at relatively low concentrations of dodecane becomes less effective. Consequently, this leads to a positive volume of mixing. Contrary to 1-decanol + heptane system, for ethanol + heptane and 2-methyl-2-butanol + heptane mixtures, excess molar volume is positive over the whole composition range (Fig. 7). With increasing temperature the volume effect of mixing increases and the maximum of $V^E(x_{\mathrm{alcohol}})$ isotherms moves toward lower concentration of alcohol. With increasing pressure the opposite effect is observed.

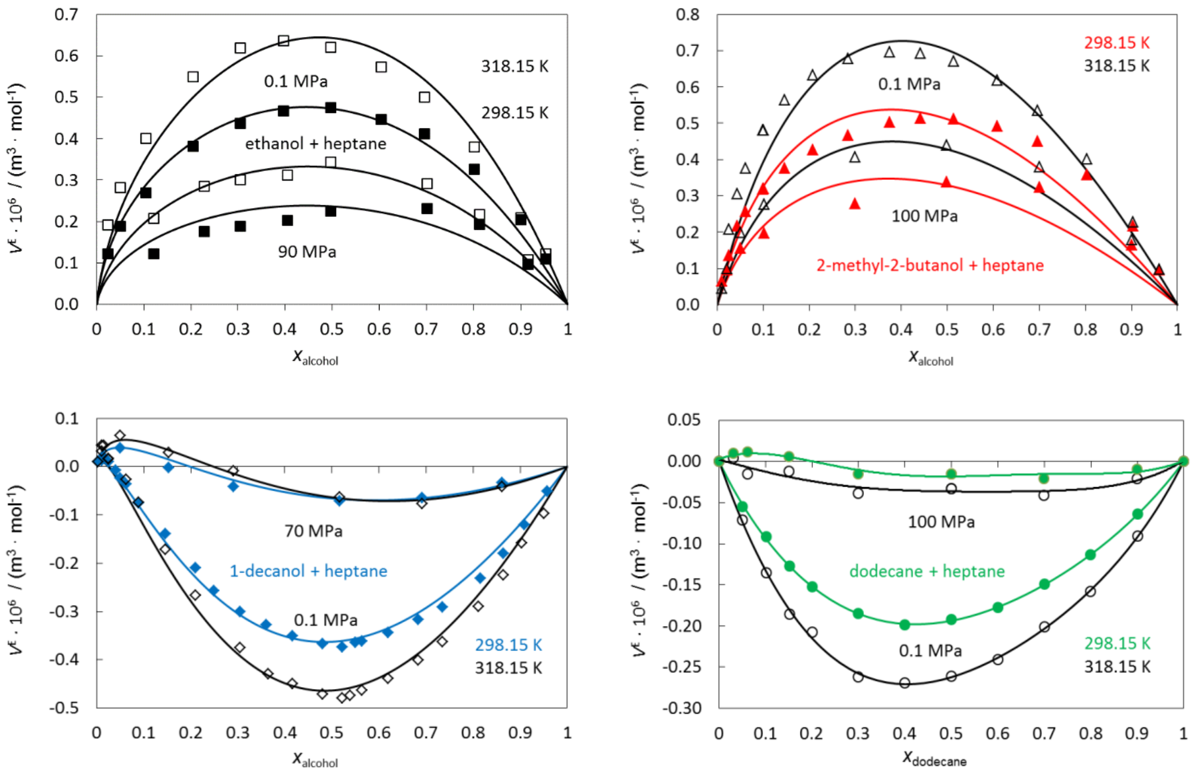

Fig. 7. The effect of temperature and pressure on concentration dependence of the excess molar volume (V^E) of: ethanol + heptane [45], 2-methyl-2-butanol + heptane [91], dodecane + heptane [88], and 1-decanol + heptane [89]; *x* denotes mole fraction

Rys. 7. Wpływ temperatury i ciśnienia na stężeniową zależność nadmiarowej objętości molowej (V^E) dla: etanol + heptan [45], 2-metylo-2-butanol + heptan [91], dodekan + heptan [88] i 1-dekanol + heptan [89]; *x* oznacza ułamek molowy

The excess molar heat capacity isotherms of alcohol + heptane mixtures are evidently asymmetric with maxima shifted toward higher alcohol concentrations (Fig. 8). With increasing temperature excess molar heat capacity of alcohol + heptane mixtures increases. In the pressure range of investigations, the effect of pressure of the excess molar heat capacity is negligible. At low concentration of alcohol, the isobars of excess heat capacities cross each other. Moreover, in the temperature range characteristic for each alcohol, the excess molar heat capacity is S-shaped with small negative values at low alcohol concentrations. In the temperature range under study, this effect is the most visible for 2-methyl-2-butanol + heptane mixtures at both atmospheric and high pressures (Fig. 8).

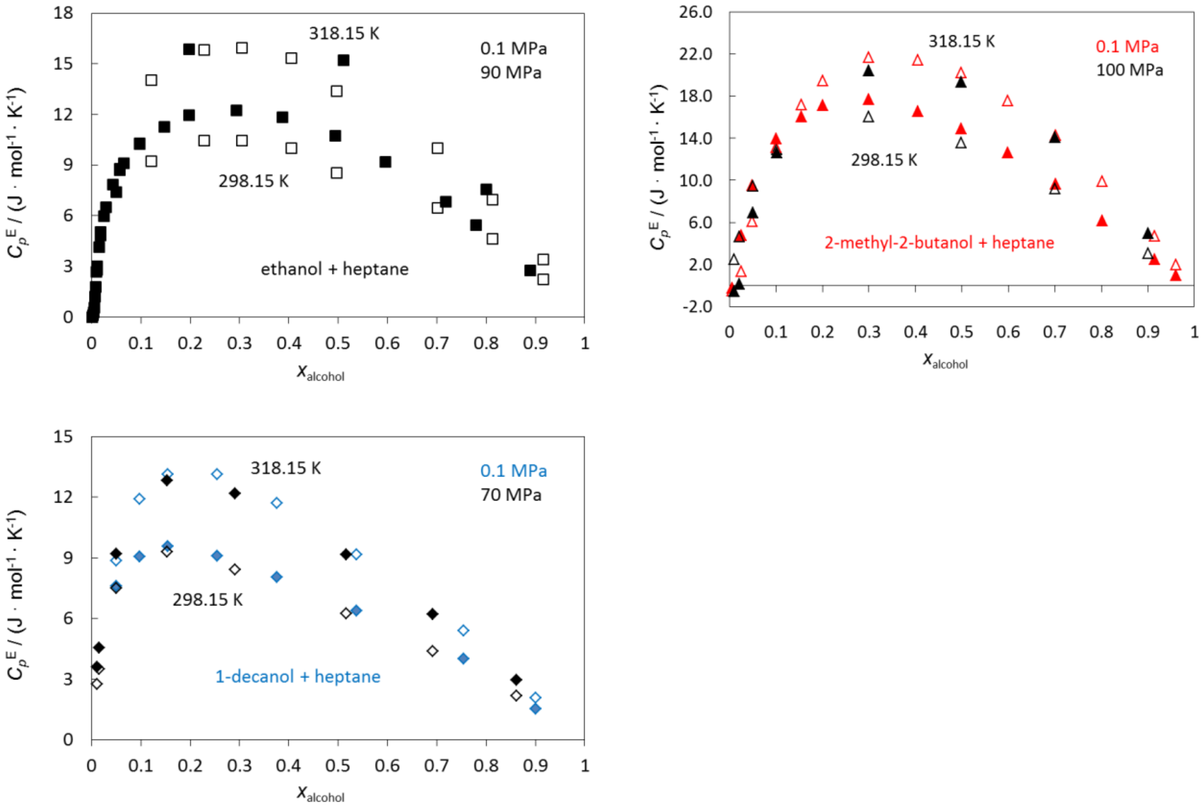

Fig. 8. The effect of temperature and pressure on concentration dependence of the excess molar isobaric heat capacity (C_p^E) of: ethanol + heptane [45, 93, 94], 2-methyl-2-butanol + heptane [91,92], and 1-decanol + heptane [50, 89]; x denotes mole fraction

Rys. 8. Wpływ temperatury i ciśnienia na stężeniową zależność nadmiarowej molowej izobarycznej pojemności cieplnej (C_p^E) dla: etanol + heptan [45, 93, 94], 2-metylo-2-butanol + heptan [91,92] i 1-dekanol + heptan [50, 89]; x oznacza ułamek molowy

5.5. Nonlinearity parameter *B*/*A*

The second-order nonlinearity parameter B/A (i.e. the ratio of quadratic B to linear A term in the Taylor series expansion of equation of state $p = p\ (\rho, S)$) is a basic measure of acoustic nonlinearity properties of materials and determines distortion of a finite amplitude wave propagating in the liquid. Therefore B/A is very important and interesting both from theoretical and practical point of view in many areas. This is especially true for underwater acoustics and modern medical applications of ultrasound [95, 96]. The B/A values can also be an important information's source about molecular structure; it can also be treated as a complementary parameter in the general characterization of the liquids [97, 98]. For determination of the acoustic nonlinearity parameter B/A various methods have been proposed. One of them is so-called classical thermodynamic method proposed by Beyer [99, 100] which is based on the expression

$$B/A = 2\cdot\rho\cdot c\cdot\left(\frac{\partial c}{\partial p}\right)_S . \qquad (13)$$

This expression (isentropic partial derivative is inconvenient to retain) can be resolved into much more convenient isothermal and isobaric term,

$$B/A = 2\cdot\rho\cdot c\cdot\left(\frac{\partial c}{\partial p}\right)_T + 2\cdot c\cdot T\cdot\frac{\alpha_p}{c_p}\left(\frac{\partial c}{\partial T}\right)_p , \qquad (14)$$

where $(\partial c/\partial p)_T$ and $(\partial c/\partial T)_p$ are, respectively, the change of the speed of sound with pressure at constant temperature and the change of the speed of sound with temperature at constant pressure. This expression can be rewritten in the form

$$B/A = (B^{'}/A) + (B^{''}/A) , \qquad (15)$$

i.e., as the sum of two terms. The first term shows contribution to *B*/*A* from pressure changes whereas the second term shows contribution to *B*/*A* from temperature changes. In principle, the method is based on the speed of sound measurements as function of pressure and temperature and application of the acoustic way to determination of related thermodynamic properties (see Sec. 2). The $(\partial c/\partial p)_T$ and $(\partial c/\partial T)_p$ derivative can be obtained by differentiation of the equation used for smoothing out the *c*, *p* and *T* values. Thermodynamic method seems very reliable method for determination of the nonlinearity parameter *B*/*A*; however, the quality of the speed of sound data is crucial to obtain reliable values of *B*/*A* [98]. The reliability of the results is confirmed in the case of 1,3-butanediol by excellent accordance of the *B*/*A* values (298.15 K and 0.1 MPa) obtained by thermodynamic method [98] and by three other different methods [101, 102]. It is very important because uncertainty of the determinations of *B*/ *A* is one of the crucial problems taking into account the diversity of the methods reported in the literature.

Investigations of *B*/*A* in the case of the lower alkanediols show that the obtained *B*/*A*(*p,T*) values are typical and similar to those reported for mostly organic liquids. The lowest nonlinearity parameters show α,ω-diols (1,3-propanediol and 1,4-butanediol, whereas the highest show 1,2-diols (1,2-propanediol and 1,2-butanediol). The values of *B*/*A* are very slightly temperature dependent but decrease significantly and nonlinearly with the increasing pressure. Moreover, the difference between *B*/*A* values decreases with the increasing pressure.

The first studies were also carried out by us for ILs. To date, however, the *B*/*A* (*p,T*) values were reported for one IL only [87], namely [C_2C_1im][NTf_2]. While the *B*/*A* decreases nonlinearly with increasing pressure, the *B*/*A* values are insensitive to temperature in the investigated range (Fig. 9).

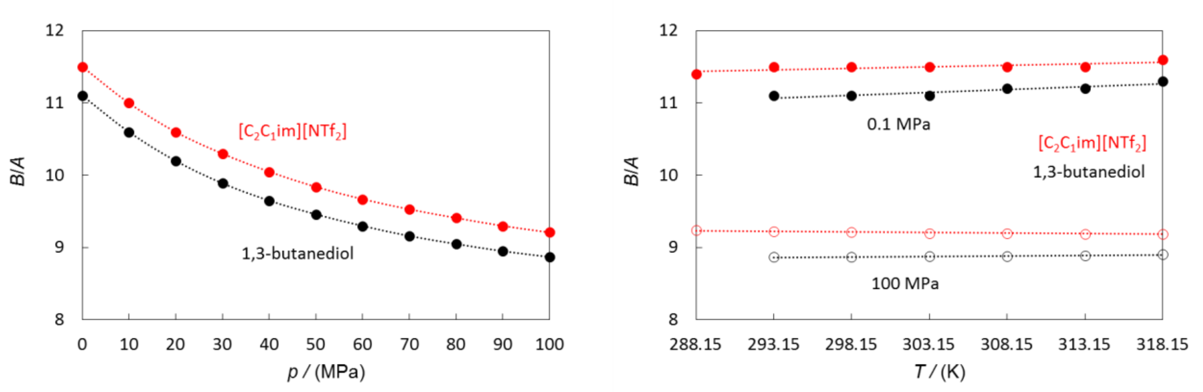

Fig. 9. Dependence of B/A on pressure (p) at temperature 298.15 K for 1,3-butanediol [98] and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[C_2C_1im][NTf_2]$ [87] as well as dependence of B/A on temperature (T) for 1,3-butanediol [98] and $[C_2C_1im][NTf_2]$ [87] at pressure 0.1 MPa (full symbols) and 100 MPa (empty symbols). Lines – arbitrary

Rys. 9. Zależność B/A od ciśnienia (p) w temperaturze 298.15 K dla 1,3-butanodiolu [98] i bis-(trifluorometylosulfonylo)imidu 1-etylo-3-metyloimidazoliowego $[C_2C_1im][NTf_2]$ [87] oraz zależność B/A od temperatury (T) dla 1,3-butanodiolu [98] i $[C_2C_1im][NTf_2]$ [87] pod ciśnieniem 0.1 MPa (pełne symbole) i 100 MPa (puste symbole). Linie – arbitralnie

It appears that in the aspect of nonlinear properties related to the propagation of the ultrasonic waves, the behavior of the tested IL does not differ from behaviour of molecular organic liquids. This applies to both associated molecular liquids [97, 98, 103-106] and non-associated molecular liquids [107, 108]. Although it can be supposed that such behaviour will be observed also for other ILs, obtained result does not allow generalization. Due to the fact that ILs are materials which interest is still growing, it seems highly desirable to study B/A for other types of ILs.

5.6. Summary

Usefulness and reliability of acoustic method to evaluate the consistent sets of thermodynamic properties are shown. This applies to both atmospheric and high pressures. In the latter case there is especially important and difficult to overestimate because the demand for this type of thermodynamic data is very high. The advantages of this method, i.e. relative simplicity, rapidity and accuracy, make it really a very attractive and reliable alternative to the other known methods, for all types of homogenous liquid systems.

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