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Research Paper

Are the Heat Capacities of Liquids Calculated from Speeds of Sound and $p_\rho T$ Relationships Reliable? A Comparison with the Reference Values and a Discussion of the Uncertainties

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Recent advances in the construction of speed of sound meters made high-accuracy routine measurements possible in laboratories non-specialized in physical acoustics. Reliable values of the isentropic compressibility can be obtained from speeds of sound and densities of liquids using the Laplace formula. Strict thermodynamic relationships connect the isentropic compressibility of a medium and its density as a function of temperature and pressure with the heat capacity. These relationships result from the principles of thermodynamics and require no approximations or molecular models. In this study, the heat capacities of twelve liquids: hydrocarbons, acetonitrile, and ionic liquids were calculated from the speeds and densities taken from the literature sources. The agreement of the calculation results with the reference heat capacities, either critical values or measured calorimetrically, was satisfactory. The relative uncertainty of the calculated heat capacities was rather conservatively estimated for 5%. If the measurement procedures were optimized for heat capacity determination, better results would be attained, with the uncertainty probably smaller than 1%. Thus, the speed-and-density method is a potential alternative to classical calorimetry.

Keywords: speed of sound; density; compressibility; expansibility; calorimetry; elevated pressure.

1. Introduction

Commonly, the heat capacities of liquids are measured using calorimeters of various types. Modern calorimeters are sophisticated instruments that require specialist knowledge to be properly operated. Alternatively, heat capacity can be calculated from other material constants, such as density ρ, isobaric thermal expansibility α_p, and compressibilities: isothermal κ_T and isentropic κ_S. The following strict thermodynamic formula can be used for the specific heat capacity c_p:

$$c_p = \frac{T\alpha_p^2}{(\kappa_T - \kappa_S)\rho}, \tag{1}$$

where T is the absolute temperature. Derivation of Eq. (1) is based on the thermodynamic definitions and the Maxwell relations. Its draft was reported by REIS *et al.* (2001). It should be noted that no model assumptions or approximations have been introduced in the derivation. Thus, the only source of uncertainty in the heat capacity calculated from Eq. (1) would be uncertainties in the measured quantities reported on the right-hand side of Eq. (1).

Development of the vibrating-tube densimeters and speed of ultrasound meters in the last decades made the indirect method worthy of consideration. From among four material constants reported on the right-hand side of Eq. (1), ρ is measured directly, while the α_p and κ_T can be calculated from the density according to the definitions:

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \tag{2}$$

and

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T, \tag{3}$$

where V is volume. Either equations of state, $\rho = f(pT)$ or $V = f(Tp)$, or approximate relationships of the form

$(\partial\rho/\partial T)_p \approx (\Delta\rho/\Delta T)_p$ could be applied to this end. The fourth material constant, the isentropic compressibility defined as:

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S, \tag{4}$$

is related to the speed of sound u and density by the Laplace formula:

$$\kappa_S = \rho^{-1}u^{-2}. \tag{5}$$

The suggested method of calculations, based on the difference between the isothermal and isentropic compressibilities (Eq. (1)), seems to be rather simple. To our surprise, we could not find literature sources relevant to this method in the Web of Science database. Thus, we felt tempted to verify whether it was of practical value.

It should be noted that $V = f(pT)$ equations have been applied in the assessments of heat capacities at elevated pressures. However, the calculated quantity was not the C_p itself, but rather the change in heat capacity due to the pressure change:

$$(\partial C_p/\partial p)_T = -T\left(\partial^2 V/\partial T^2\right)_p. \tag{6}$$

In this manner, Bridgman (1912) calculated the heat capacity of water at pressures up to 1200 MPa. A modified method can be applied as well. If $C_p(T)$ and $\rho(T)$ are known at a reference pressure, usually at the atmospheric one, their pressure and temperature relationships can be obtained from the respective relationship for the speed of sound, $u(T,p)$, e.g. (Sun *et al.*, 1988; Marczak *et al.*, 2000). The $C_p(p,T)$ values of 1-hexanol determined in this way by Marczak *et al.* (2000), differed by less than −1.6% from those measured calorimetrically by Randzio *et al.* (1995). Thus, the "acoustic" values of the heat capacities and densities proved to be reliable, despite a rather complex extrapolation procedure.

Both the calculations reported in this work and those mentioned in the preceding paragraph apply the same theory. This lets us believe that the suggested calculation method is worthy of exploration.

2. Calculations

Heat capacities of twelve liquids: n-heptane, n-octane, n-nonane, n-decane, benzene, toluene, acetonitrile, 1-ethyl-3-methylimidazolium ethyl sulfate [C_2mim][$EtSO_4$], and 1-amyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imides: propyl [C_3mim][NTf_2], n-butyl [C_4mim][NTf_2], n-pentyl [C_5mim][NTf_2], and n-hexyl [C_6mim][NTf_2] at several temperatures were calculated and compared with the reference values. All data were taken from the literature sources reported in the next section. Depending on the forms of the applied equations of state, Eq. (1) was either unchanged or re-arranged in the following manner:

$$C_p = \frac{TE_p^2}{K_T - K_S}, \tag{7}$$

where C_p is the extensive heat capacity, E_p is the isobaric expansion, and K_T and K_S are the compressions, isothermal and isentropic, respectively. E_p, K_T and K_S could be obtained either directly, as the first derivatives of volume, or by a multiplication of the respective intensive functions (Eqs (2)–(4)) by volume. In practice, the volume is either the specific or molar one. Consequently, the expansion and compressions are specific or molar values, respectively. In the first case, the calculation result is the specific heat capacity, c_p, while it is its molar counterpart, $C_{p,m}$, in the second one.

The isobaric thermal expansibilities and isothermal compressibilities or their extensive counterparts were either taken directly from the literature sources that were reported later in this paper (Table 1), or they were calculated from the dependencies of density or volume on temperature and pressure (Eqs (2) and (3)). Commonly, the pressure dependencies of density were expressed by Tait equations:

$$\frac{1}{\rho} = \frac{1}{C} + A\ln\frac{B+p}{B+0.1}, \tag{8}$$

where p is in MPa, and A, B, and C were fitted coefficients. The dependencies of density on temperature T (in kelvins) were expressed as:

$$y = \sum_{i=0}^{n} a_i\,(T-\vartheta)^i, \tag{9}$$

where $y = \rho$ or $y = \ln\rho$, a_i were the regression coefficients, $n \le 3$, and ϑ was an arbitrarily chosen reference temperature. The Tait equation used for acetonitrile by Ahmadiyarov *et al.* (2021), had the following form, slightly different from Eq. (8):

$$\rho(p,T) = \frac{\rho_0(T)}{1 - C\ln\frac{B(T)+p}{B+0.1}}, \tag{10}$$

where ρ_0 (the density at atmospheric pressure) was expressed by Eq. (9) with $n = 3$ and $\vartheta = 0$, while

$$B(T) = \sum_{i=0}^{2} B_i T^i \tag{11}$$

with the regression coefficients C and B_i.

Densities of hydrocarbons and their heat capacities were calculated using the "Fluid property" module implemented in the *NIST Chemistry WebBook* (Linstrom, Mallard, 2021). These quantities are denoted as "NIST" from here on.

Table 1. Molar isobaric heat capacities of twelve liquids at atmospheric pressure calculated in this work compared with the measurement results reported in literature sources or critical values from the *NIST Chemistry WebBook* (Linstrom, Mallard, 2021), absolute (U) and relative (U_{rel}) uncertainties, and calculation errors: absolute $\Delta C_{p,m}$ and relative $\delta C_{p,m}$.

Substance	T [K]	$C_{p,m}$ [J/(K·mol)]	$U(C_{p,m})$ [J/(K·mol)]	$U_{\mathrm{rel}}(C_{p,m})$ [%]	$C_{p,m}(\mathrm{lit})$ [J/(K·mol)]	$U(C_{p,m}(\mathrm{lit}))$ [J/(K·mol)]	$U_{\mathrm{rel}}(C_{p,m}(\mathrm{lit}))$ [%]	$\Delta C_{p,m}$ [J/(K·mol)]	$\delta C_{p,m}$ [%]	References		
										Density	Speed	Heat capacity
Heptane	293.15	219.7	5.5	2.5	222.6	4.5	2.0	–2.9	–1.3	NIST	Dzi[a]	NIST
Octane	293.15	218.5	5.4	2.5	252.3	5.0	2.0	–33.9	–13.4	NIST	Nat[a]	NIST
		212.9	5.7	2.7				–39.4	–15.6	NIST	Gon,Com[a]	
Nonane	293.15	279.8	4.4	1.6	280.8	5.6	2.0	–1.0	–0.4	NIST	Lag[a]	NIST
Decane	293.15	309.0	8.9	2.9	309.3	6.2	2.0	–0.3	–0.1	NIST	Lun[a]	NIST
Benzene	293.15	132.2	3.3	2.5	132.3	6.6	5.0	–0.1	–0.1	NIST	Sun[a]	NIST
		132.7	3.3	2.5				0.4	0.3	NIST	Dzi[a]	
		132.8	3.3	2.5				0.5	0.4	NIST	Tak[a]	
		133.0	3.3	2.5				0.7	0.5	NIST	Ern[a]	
Toluene	293.15	153.7	1.9	1.3	155.3	0.8	0.5	–1.5	–1.0	NIST	Tak[a]	NIST
Acetonitrile	293.15	88.9	0.8	0.9	90.60	0.14	0.2	–1.7	–1.8	Akh[b]	Gep[a]	Wal
	298.15	89.0	0.6	0.7	91.61	n/a		–2.6	–2.8	Akh[b]	Gep[a]	Che
					90.93	0.14	0.15	–1.9	–2.1			Wal
					90.6	n/a		–1.6	–1.7			Hov
					90.03	0.90	1.0	–1.0	–1.1			Tam
					89.62	n/a		–0.6	–0.7			Tja
	303.15	89.3	0.6	0.7	91.28	0.14	0.15	–2.0	–2.2	Akh[b]	Gep[a]	Wal
$[C_2mim][EtSO_4]$	293.15	376	13	3.4	388	19	5.0	–12.2	–3.1	NdC[c]	Góm[a]	Ge
	303.15	383	13	3.4	391	20	5.0	–7.8	–2.0	NdC[c]	Góm[a]	Ge
	313.15	388	13	3.4	398	20	5.0	–9.6	–2.4	NdC[c]	Góm[a]	Ge
$[C_3mim][NTf_2]$	298.15	538	6	1.2	534.9	0.5	0.1	3.6	0.7	Esp[c]	Zor[d]	Roc
$[C_4mim][NTf_2]$	293.15	616	19	3.1	595	30	5.0	20.8	3.5	NdC[c]	Zor[d]	Ge
	298.15	563	16	2.8	599	30	5.0	–35.8	–6.0	NdC[c]	Zor[d]	Ge
					565.9	0.6	0.1	–2.7	–0.5			Roc
	298.15	542	20	3.8	599	30	5.0	–57.4	–9.6	GdA[c]	GdA[d]	Ge
					565.9	0.6	0.1	–24.3	–4.3			Roc
$[C_5mim][NTf_2]$	298.15	607	7	1.2	595.6	0.5	0.1	11.6	1.9	Esp[c]	Zor[d]	Roc
$[C_6mim][Ntf_2]$	298.15	593	45	7.5	629.4	1.2	0.2	–36.3	–5.8	GdA[c]	Zor[d]	Roc

References: Akh – (Akhmadiyarov *et al.*, 2021), Che – (Checoni, Francesconi, 2007), Com – (de Cominges *et al.*, 2002), Dzi – (Dzida *et al.*, 2006), Ern – (Ernst *et al.*, 1992), Esp – (Esperança *et al.*, 2006), GdA – (Gomes de Azevedo *et al.*, 2005), Ge – (Ge *et al.*, 2008), Gep – (Geppert-Rybczyńska, Sitarek, 2014), Góm – (Gómez *et al.*, 2006), Gon – (González *et al.*, 2003), Hov – (Hovorka *et al.*, 1999), Lag – (Lago *et al.*, 2006), Lun – (Luning Prak *et al.*, 2017), Nat – (Nath, 1997), NdC – (Nieto de Castro *et al.*, 2010), Roc – (Rocha *et al.*, 2012), Sun – (Sun *et al.*, 1987), Tak – (Takagi, Teranishi, 1987), Tam – (Tamura *et al.*, 1994), Tja – (Tjahjono, Garland, 2008), Wal – (Waliszewski, Piekarski, 2010), Zor – (Zorębski *et al.*, 2016).

[a] Single measured value; [b] calculated from Eq. (10); [c] calculated from Eqs (8) and (9); [d] calculated from Eq. (9): $y = u$.

The isentropic compressibilities were calculated from the speeds of sound using Eq. (4). In the calculations, either the measured speeds were used, or those obtained from polynomials analogous to Eq. (9) with $y = u$.

The uncertainties of the calculated heat capacities were estimated according to the rules of the calculus of errors (Czermiński *et al.*, 1990). The combined uncertainty of C_p obtained from Eq. (7) was given by:

$$\begin{aligned} U(C_p) = {} & \left|\frac{\partial C_p}{\partial T}\right|_{E_p,K_T,K_S} U(T) \\ & + \left|\frac{\partial C_p}{\partial E_p}\right|_{T,K_T,K_S} U(E_p) \\ & + \left|\frac{\partial C_p}{\partial K_T}\right|_{T,E_p,K_S} U(K_T) \\ & + \left|\frac{\partial C_p}{\partial K_S}\right|_{T,E_p,K_T} U(K_S), \end{aligned} \tag{12}$$

where $U(T)$, $U(E_p)$, $U(K_T)$, and $U(K_T)$ denote the uncertainties of temperature, thermal isobaric expansion, isothermal compression, and isentropic compression, respectively, and:

$$\left|\frac{\partial C_p}{\partial T}\right|_{E_p,K_T,K_S} = \frac{E_p^2}{K_T - K_S}, \tag{13}$$

$$\left|\frac{\partial C_p}{\partial E_p}\right|_{T,K_T,K_S} = \frac{2TE_p}{K_T - K_S}, \tag{14}$$

$$\left|\frac{\partial C_p}{\partial K_T}\right|_{T,E_p,K_S} = \left|\frac{\partial C_p}{\partial K_S}\right|_{T,E_p,K_T} = \frac{TE_p^2}{(K_T - K_S)^2}. \tag{15}$$

In the combined uncertainty calculations, we used the measurement uncertainties claimed by the authors of the reference sources. If the uncertainties were not stated directly, we estimated their values from the number of significant digits in the coefficients of the fitted equations. The relative uncertainty was defined conventionally as:

$$U_{\mathrm{rel}}(C_p) = \frac{U(C_p)}{C_p}. \tag{16}$$

3. Results

The calculated molar heat capacities and literature values with their uncertainties are reported in Table 1. The absolute and relative errors were defined as:

$$\Delta C_{p,m} = C_{p,m} - C_{p,m}(\mathrm{lit}) \tag{17}$$

and

$$\delta C_{p,m} = \frac{\Delta C_{p,m}}{C_{p,m}(\mathrm{lit})}, \tag{18}$$

respectively, where $C_{p,m}(\mathrm{lit})$ is the "true" heat capacity. The latter were either critical values taken from the *NIST Chemistry WebBook* (Linstrom, Mallard, 2021), or results of calorimetric measurements.

4. Discussion

The calculated molar heat capacities are in good agreement with the values measured calorimetrically and those reported in the *NIST Chemistry WebBook* (Linstrom, Mallard, 2021) (Fig. 1). The result for n-octane was not considered for the reason that will be discussed later in this section. The scatter is bigger for the ionic liquids than for the other substances. That is justified by the fact that the densities, speeds of sound, and heat capacities of the ionic liquids applied in this comparison were just measurement results, each reported by one group of researchers, rather than critical values based on several sets of the experimental data. For example, the agreement between the heat capacity of [C_4mim][Ntf_2] at temperature 298.15 K calculated from the densities and speeds reported by Nieto de Castro *et al.* (2010) and Zorębski *et al.* (2016), respectively, and that measured by Rocha *et al.* (2012), is almost perfect. The relative difference of −0.5% is within the relative uncertainty limits of the calculated value, equal to 2.8%. The heat capacities calculated from the densities and speeds reported by Gomes de Azevedo *et al.* (2005), differ from the measured values of Rocha *et al.* (2012) by −4.3%. To facilitate the comparison, these and three other heat capacity values were plotted in Fig. 2. It seems reasonable to suppose that the impurities in the chemicals used in particular experiments could contribute significantly to the measurement errors. Contrary to the uncertainty due to the apparatus characteristics, this effect is difficult or even impossible to estimate.

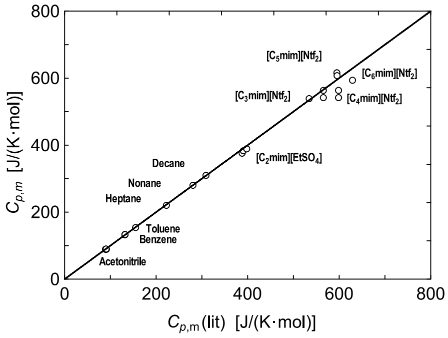

Fig. 1. Molar heat capacities at atmospheric pressure: literature values vs those calculated in this work (for the references see Table 1). The line represents a hypothetic ideal case where the two values for a substance are identical.

The highest relative difference between the calculated and measured heat capacity was −9.6% for [C_4mim][Ntf_2] at 298.15 K (Table 1). In this case, the density and speed reported by Gomes de Azevedo *et al.* (2005), were used in the calculations, while the $C_{p,m}$ = 599 J/(K·mol) was reported by Ge *et al.* (2008). The latter authors estimated the "instrument uncertainty" for 5% in their calorimetric measurements. The 5% added to the 3.8% uncertainty

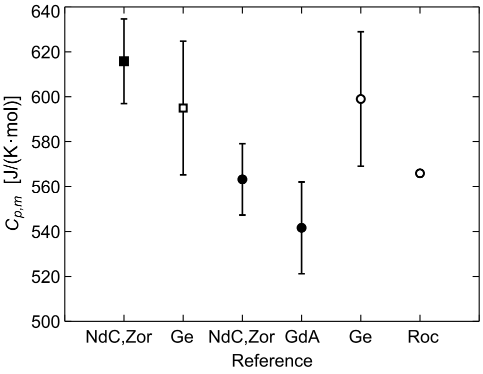

Fig. 2. Molar heat capacity of [C_4mim][Ntf_2] calculated from the densities and speeds of sound (filled symbols) and measured calorimetrically (empty symbols). Squares – T = 293.15 K, circles – T = 298.15 K. References: NdC – (Nieto de Castro *et al.*, 2010), Zor – (Zorębski *et al.*, 2016), Ge – (Ge *et al.*, 2008), GdA – (Gomes de Azevedo *et al.*, 2005), Roc – (Rocha *et al.*, 2012).

of the calculated heat capacity gives ca. 9% combined uncertainty of the difference between the two $C_{p,m}$ values. That fits quite well with the observed relative difference. Moreover, the heat capacity of (565.9 ± 0.6) J/(K · mol), measured by Rocha *et al.* (2012), also differs considerably from that of Ge *et al.* (2008). That supports the idea that the differences due to the impurities in the investigated liquid samples cannot be neglected.

The results for acetonitrile, reported in Fig. 3, evidence that the calculated heat capacities are very close to the measured ones. However, a slight systematic shift towards lower values is observed. This tendency seems to be predominant in the majority of the results, which is illustrated by the histogram in Fig. 4.

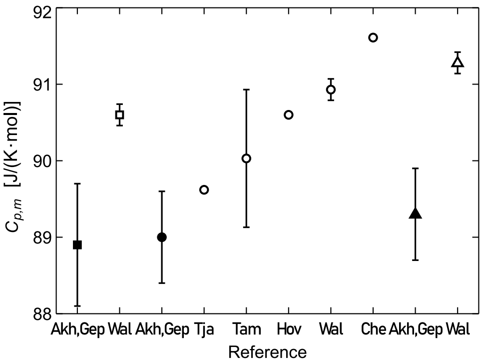

Fig. 3. Molar heat capacity of acetonitrile calculated from the densities and speeds of sound (filled symbols) and measured calorimetrically (empty symbols). Squares – T = 293.15 K, circles – T = 298.15 K, triangles – T = 303.15 K. References: Akh – (Akhmadiyarov *et al.*, 2021), Gep – (Geppert-Rybczyńska, Sitarek, 2014), Wal – (Waliszewski, Piekarski, 2010), Tja – (Tjahjono, Garland, 2008), Tam – (Tamura *et al.*, 1994), Hov – (Hovorka *et al.*, 1999), Che – (Checoni, Francesconi, 2007).

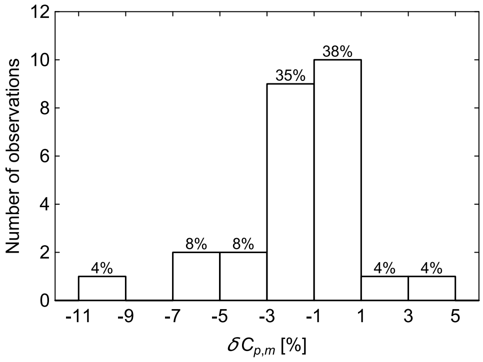

Fig. 4. Histogram of the discrepancies between the calculated molar heat capacities and the reference values reported in the literature sources.

Ten out of 26 calculated heat capacities is equal to the reference values within ±1% of the C_p. As many as 14 is smaller by more than 1%, while just two are bigger by more than 1%. That probably results from systematic errors in the estimated isothermal compressibilities. For example, the density of acetonitrile was measured by Akhmadiyarov *et al.* (2021), at pressures from 0.1 MPa up to 50 MPa. The lowest elevated pressure was 1 MPa, ten times higher than the atmospheric one. The next pressure, 5 MPa, was fifty times higher. Thus, the fitted Eq. (10) for the dependence of density on pressure could be not fully reliable for low pressures due to the lack of experimental results in this pressure range. In particular, this flaw would influence the pressure derivative of density, i.e. the calculated isothermal compression, and, consequently, the isothermal compressibility (cf. Eq. (3)). If the true isothermal compressibility of acetonitrile was lower only by 0.9% than the estimated value, i.e. $1.1319 \cdot 10^{-9}$ Pa^{-1} at 298.15 K rather than $1.1418 \cdot 10^{-9}$ Pa^{-1} used in the calculations, then the obtained heat capacity would be equal to the calorimetric result, 91.61 J/(K · mol) (Checoni, Francesconi, 2007), which was the highest one from among five compared in this study. Smaller corrections in κ_T would be sufficient for matching the calorimetric data reported by Hovorka *et al.* (1999), Tamura *et al.* (1994), Tjahjono and Garland (2008), and Waliszewski and Piekarski (2010).

From the generally good results, the exception is that for octane. The NIST heat capacity (Linstrom, Mallard, 2021) was significantly higher than those calculated from the speed of sound: by 13.4% (speeds reported by Nath (1997)) and by 15.6% (speeds measured by de Cominges *et al.* (2002) and González *et al.* (2003)). However, the speeds of sound in octane show a similar discrepancy. The calculated NIST value of 1166 m/s is much lower than the experimental speeds: 1188.6 m/s (Nath, 1997) and 1193 m/s (de Cominges *et al.*, 2002; González *et al.*, 2003) at 293.15 K. The second result is even outside the limits of the declared NIST uncertainty, ±2% of the speed value.

Moreover, the speed of sound in octane interpolated from the NIST speeds in heptane, nonane and decane is 1186 m/s rather than 1166 m/s. The former agrees well with the experimental data of (Nath, 1997), and only slightly worse with those of (de Cominges *et al.*, 2002; González *et al.*, 2003). Evidently, the thermodynamic data for octane obtained from the NIST equation of state were not sufficiently consistent for the tested application. Thus, the heat capacity of octane was not reported in the figures. It must be stressed again that the discrepancy is not caused by a flaw in the method of calculations, because the latter is based on strict thermodynamic relationships.

The discussion of the calculation results would be incomplete without pointing to the limitations of the method. It is easy to notice that Eq. (1) fails for liquids of null thermal expansion. Water ^1H_2O at $T = 277.13$ K is a good example of such a substance. In such case $\alpha_p = 0$ and $\kappa_T = \kappa_S$, and Eq. (1) gives the 0/0 expression, which is an indeterminate form. An application of L'Hôpital's rule could help to evaluate C_p. However, the uncertainty of such an assessment would be higher, because of the calculation procedure consisting in the determination of temperature derivatives of thermal expansibility and isothermal and isentropic compressibilities. Fortunately, no common liquid except water shows such behaviour.

Other thermodynamic functions can be obtained using the discussed method as well. For example, the isochoric heat capacity, C_V, can be calculated from the isobaric heat capacity with the following strict thermodynamic relationship:

$$C_V = \frac{C_p}{\gamma}, \tag{19}$$

where γ is the adiabatic index given by:

$$\gamma = \frac{\kappa_T}{\kappa_S}. \tag{20}$$

The possibility of simultaneous determination of C_p and C_v is an advantage of the discussed method over the classical calorimetric measurements.

5. Conclusions

1) The isobaric heat capacity of a liquid can be calculated with reasonable uncertainty from the experimental speed of sound and the pressure and temperature dependencies of the density using strict thermodynamic relationships.
2) The uncertainty of the calculated heat capacity, estimated from Eq. (12), ranged from 0.7% to 7.5%. The comparison of the calculated and literature C_p values suggests that 5% is a safe estimation of the uncertainty for careful measurements with a modern speed-of-sound meter and oscillating-tube densimeter.
3) Although the datasets used in these calculations were not optimized for heat capacity determination, the calculated C_p values were acceptable. A 1% relative uncertainty of C_p can be probably attained if the temperature and pressure intervals between the measured densities are smaller. The smaller are the temperature and pressure steps in the measurements, the better are the α_p and κ_T estimations.
4) The absolute accuracy of the density determination is less important than the high precision. A contribution to the combined uncertainty of C_p due to uncertainty of density of the order of 0.1 $\text{kg}\cdot\text{m}^{-3}$ is negligible.
5) Speeds of sound measured with an uncertainty of 1 m/s or even slightly worse are sufficiently good to be used in the calculations.
6) Apart from the isobaric heat capacity, other thermodynamic functions can be calculated by the suggested method as well, in particular the isochoric heat capacity and the adiabatic index. This is an advantage of the analyzed method over the classical calorimetric measurements.

References

1. Akhmadiyarov A.A., Marczak W., Petrov A.A., Rakipov I.T. (2021), Measurements of density at elevated pressure – a vibrating-tube densimeter calibration, uncertainty assessment, and validation of the results, *Journal of Molecular Liquids*, **336**: 116196, doi: 10.1016/j.molliq.2021.116196.
2. Bridgman P.W. (1912), Thermodynamic properties of liquid water to 80° and 12000 kgm, *Proceedings of the American Academy of Arts and Sciences*, **48**(9): 309–362, https://www.jstor.org/stable/20022832.
3. Checoni R.F., Francesconi A.Z. (2007), Measurements of the molar heat capacities and excess molar heat capacities for acetonitrile + diethylamine or sec-butylamine mixtures at various temperatures and atmospheric pressure, *Journal of Solution Chemistry*, **36**(7): 913–922, doi: 10.1007/s10953-007-9155-0.
4. de Cominges B.E. *et al.* (2002), Temperature dependence of thermophysical properties of octane + 1-butanol system, *Journal of Thermal Analysis and Calorimetry*, **70**(1): 217–227, doi: 10.1023/A:1020626205538.
5. Czermiński J., Iwasiewicz A., Paszek Z., Sikorski A. (1990), *Statistical Methods in Applied Chemistry*, PWN – Polish Scientific Publishers, Warszawa; Elsevier, Amsterdam, Oxford, New York, Tokyo.
6. Dzida M., Chorążewski M., Zorębski M., Mańka R. (2006), Modifications of a high pressure device for speed of sound measurements in liquids, *Journal de Physique IV France*, **137**: 203–207, doi: 10.1051/jp4:2006137042.

7. Ernst S., Marczak W., Manikowski R., Zorębski E., Zorębski M. (1992), A sing-around apparatus for group velocity measurements in liquids. Testing by standard liquids and discussion of the errors, *Acoustisc Letters*, **15**(7): 123–130.

8. Esperança J.M.S.S., Visak Z.P., Plechkova N.V., Seddon K.R., Guedes H.J.R., Rebelo L.P.N. (2006), Density, speed of sound, and derived thermodynamic properties of ionic liquids over an extended pressure range. 4. [C$_3$mim][NTf$_2$] and [C$_5$mim][NTf$_2$], *Journal of Chemical & Engineering Data*, **51**(6): 2009–2015, doi: 10.1021/je060203o.

9. Geppert-Rybczyńska M., Sitarek M. (2014), Acoustic and volumetric properties of binary mixtures of ionic liquid 1-butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide with Acetonitrile and Tetrahydrofuran, *Journal of Chemical & Engineering Data*, **59**(4): 1213–1224, doi: 10.1021/je400781b.

10. Ge R., Hardacre C., Jacquemin J., Nancarrow P., Rooney D.W. (2008), Heat capacities of ionic liquids as a function of temperature at 0.1 MPa. Measurement and prediction, *Journal of Chemical & Engineering Data*, **53**(9): 2148–2153, doi: 10.1021/je800335v.

11. Gomes de Azevedo R. *et al.* (2005), Thermophysical and thermodynamic properties of ionic liquids over an extended pressure range: [bmim][NTf$_2$] and [hmim][NTf$_2$], *The Journal of Chemical Thermodynamics*, **37**(9): 888–899, doi: 10.1016/j.jct.2005.04.018.

12. Gómez E., González B., Calvar N., Tojo E., Domínguez Á. (2006), Physical properties of pure 1-ethyl-3-methylimidazolium ethylsulfate and its binary mixtures with ethanol and water at several temperatures, *Journal of Chemical & Engineering Data*, **51**(6): 2096–2102, doi: 10.1021/je060228n.

13. González B., Dominguez A., Tojo J. (2003), Viscosities, densities and speeds of sound of the binary systems: 2-propanol with octane, or decane, or dodecane at T = (293.15, 298.15, and 303.15) K, *The Journal of Chemical Thermodynamics*, **35**(6): 939–953, doi: 10.1016/S0021-9614(03)00047-8.

14. Hovorka Š., Roux A.H., Roux-Desgranges G., Dohnal V. (1999), Limiting partial molar excess heat capacities and volumes of selected organic compounds in water at 25°C, *Journal of Solution Chemistry*, **28**(12): 1289–1305, doi: 10.1023/A:1021743907228.

15. Lago S., Giuliano Albo P., Madonna Ripa D. (2006), Speed-of-sound measurements in n-nonane at temperatures between 293.15 and 393.15 K and at pressures up to 100 MPa, *International Journal of Thermophysics*, **27**(4): 1083–1094, doi: 10.1007/s10765-006-0079-5.

16. Linstrom P.J., Mallard W.G. [Eds] (2021), *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, National Institute of Standards and Technology, Gaithersburg MD 20899, accessed: 1/07/2020–25/04/2021, doi: 10.18434/T4D303.

17. Luning Prak D., Lee B., Cowart J., Trulove P. (2017), Density, viscosity, speed of sound, bulk modulus, surface tension, and flash point of binary mixtures of butylbenzene + linear alkanes (n-Decane, n-Dodecane, n-Tetradecane, n-Hexadecane, or n-Heptadecane) at 0.1 MPa, *Journal of Chemical & Engineering Data*, **62**(1): 169–187, doi: 10.1021/acs.jced.6b00542.

18. Marczak W., Dzida M., Ernst S. (2000), Determination of the thermodynamic properties of 1-propanol and 1-hexanol from speed of sound measurements under elevated pressures, *High Temperatures – High Pressures*, **32**: 283–292, doi: 10.1068/htwu248.

19. Nath J. (1997), Speeds of sound in and isentropic compressibilities of (n-butanol + n-pentane, or n-hexane, or n-heptane, or n-octane, or 2,2,4-trimethylpentane, or carbon tetrachloride) at T = 293.15 K, *The Journal of Chemical Thermodynamics*, **29**(8): 853–863, doi: 10.1006/jcht.1997.0200.

20. Nieto de Castro C. *et al.* (2010), Studies on the density, heat capacity, surface tension and infinite dilution diffusion with the ionic liquids [C$_4$mim][NTf$_2$], [C$_4$mim][dca], [C$_2$mim][EtOSO$_3$] and [Aliquat][dca], *Fluid Phase Equilibria*, **294**(1–2): 157–179, doi: 10.1016/j.fluid.2010.03.010.

21. Randzio S.L., Grolier J.-P.E., Quint J.R. (1995), Thermophysical properties of 1-hexanol over the temperature range from 303 K to 503 K and at pressures from the saturation line to 400 MPa, *Fluid Phase Equilibria*, **110**(1–2) 341–359, doi: 10.1016/0378-3812(95)02761-3.

22. Reis J., Blandamer M., Davis M., Douhéret G. (2001), The concepts of non-Gibbsian and non-Lewisian properties in chemical thermodynamics, *Physical Chemistry Chemical Physics*, **3**(8): 1465–1470, doi: 10.1039/B009512P.

23. Rocha M.A.A., Bastos M., Coutinho J.A.P., Santos L.M.N.B.F. (2012), Heat capacities at 298.15 K of the extended [C$_n$C$_1$im][Ntf$_2$] ionic liquid series, *The Journal of Chemical Thermodynamics*, **53**: 140–143, doi: 10.1016/j.jct.2012.04.025.

24. Sun T.F., Kortbeek P.J., Trappeniers N.J., Biswas S.N. (1987), Acoustic and thermodynamic properties of benzene and cyclohexane as a function of pressure and temperature, *Physics and Chemistry of Liquids*, **16**(3): 163–178, doi: 10.1080/00319108708078516.

25. Sun T.F., Ten Seldam C.A., Kortbeek P.J., Trappeniers N.J., Biswas S.N. (1988), Acoustic and thermodynamic properties of ethanol from 273.15 to 333.15 K and up to 280 MPa, *Physics and Chemistry of Liquids*, **18**(2): 107–116, doi: 10.1080/00319108808078584.

26. Takagi T., Teranishi H. (1987), Ultrasonic speed in compressed liquid by a sing-around method, *The Journal of Chemical Thermodynamics*, **19**(12): 1299–1304, doi: 10.1016/0021-9614(87)90007-3.

27. Tamura K., Murakami S., Akagi Y., Fukumori M., Kawasaki Y. (1994), Thermodynamic properties of binary mixtures: hexamethylphosphoric triamide + a polar liquid at 25°C, *Journal of Solution Chemistry*, **23**(9): 263–273, doi: 10.1007/BF00973550.

28. Tjahjono M., Garland M. (2008), Deuterium isotope effect on molar heat capacities and apparent molar heat capacities in dilute aqueous solutions: A multichannel heat-flow microcalorimeter study, *The Journal of Chemical Thermodynamics*, **40**(11): 1600–1606, doi: 10.1016/j.jct.2008.06.008.

29. Waliszewski D., Piekarski H. (2010), Heat capacities of the mixtures of ionic liquids with acetonitrile, *The Journal of Chemical Thermodynamics*, **42**(2): 189–192, doi: 10.1016/j.jct.2009.08.002.

30. Zorębski M. *et al.* (2016), Ultrasonic relaxation study of 1-alkyl-3-methylimidazolium-based room-temperature ionic liquids: probing the role of alkyl chain length in the cation, *The Journal of Physical Chemistry B*, **120**(14): 3569–3581, doi: 10.1021/acs.jpcb.5b12635.