Thermophysical Characterization of Liquids Using Precise Density and Isobaric Heat Capacity Measurements As a Function of Pressure

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A specific methodology for determining density, isobaric thermal expansivity, isothermal and isoentropic compressibility, and isobaric and isochoric heat capacity of liquids as a function of temperature and pressure is analyzed in detail. The procedure is based on the experimental determination of both the density using the Anton Paar DMA512P vibrating tube densimeter and the isobaric heat capacity using the micro DSCII calorimeter from Setaram, which was recently adapted to operate up to 70 MPa. All properties are derived from these measurements using appropriate thermodynamic relations. To estimate the attained accuracy, densities for hexane, nonane, decane, undecane, dodecane, tridecane, tetradecane, 1-hexanol, and toluene were measured in the temperature interval of (283.15 to 323.15) K and at selected pressures between (0.1 and 60) MPa. Isobaric heat capacities for the same liquids (except toluene) were previously reported.[9] The comparison between the complete set of properties for these liquids and selected literature data shows that this methodology allows us to get an accurate description of the thermodynamic behavior of liquids as a function of temperature and pressure.

Introduction

Thermodynamic characterization of liquids has attracted much interest in the context of both industrial applications and basic knowledge of matter. On one hand, the analysis of the suitability of a liquid for a specific industrial process requires the determination of its thermodynamic properties. On the other hand, the features of a liquid on a molecular scale are closely related to its macroscopic behavior;[1] molecular models are usually defined in terms of their ability to reproduce the macroscopic properties of the considered systems.

Density, ρ, speed of sound, u, isobaric thermal expansivity, α_p, isothermal and isoentropic compressibility, κ_T and κ_S, respectively, and isobaric and isochoric molar heat capacity, $C_{p,\mathrm{m}}$ and $C_{v,\mathrm{m}}$, respectively, are frequently used for characterizing a liquid. Although there are specific experimental methods for determining each property, the common methodology is to measure a set of them and derive the other ones by using thermodynamic relations. Appropriate methods have been designed for experimental measurements of ρ and u as a function of temperature, T, and pressure, p, ($p\rho T$ or puT data) because they are obtained with high precision from several experimental techniques.[2,3] Specifically, the complete set of magnitudes can be obtained from (i) $p\rho T$ and $p_{\mathrm{ref}}C_{p,\mathrm{m}}T$ data ($C_{p,\mathrm{m}}$ is measured at a reference pressure, p_{ref} as a function of T),[4] (ii) $p\rho T$ and puT data,[5] and (iii) $p_{\mathrm{ref}}\rho$T, $p_{\mathrm{ref}}C_{p,\mathrm{m}}$T, and puT measurements using a complex procedure based on a "predictor−corrector" algorithm.[6] It has been shown that these methods provide a reliable description of the volumetric properties; however, the obtained results for heat capacities (isobaric and isochoric) are poor. Improvement was reached from (iv) $p\alpha_pT$ determinations using a specific calorimetric technique (transitiometer method) combined with $p_{\mathrm{ref}}\rho$T and $p_{\mathrm{ref}}C_pT$ data.[7] Alternatively, the same set of properties can be obtained from (v) $p\rho T$ and pC_pT measurements combined with specific thermodynamic relations.[8] This method has rarely been used because isobaric heat capacity measurements of liquids as a function of pressure have not been done both extensively and accurately. However, it appears to be the best procedure for a reliable and complete description of all above-mentioned properties.[8]

Recently, we have developed an experimental technique for the precise determination of the isobaric heat capacity of liquids under pressure.[9] The equipment is an adaptation of the atmospheric pressure calorimeter (micro DSC II from Setaram) to operate up to 70 MPa. The relative uncertainty in the determination of the isobaric molar heat capacity, $C_{p,\mathrm{m}}$ was estimated to be 0.08 % and 0.2 % at atmospheric and higher pressure, respectively, values that reflect the high accuracy of the equipment. In that work, the isobaric molar heat capacity for hexane, nonane, decane, undecane, dodecane, tridecane, tetradecane, and 1-hexanol in the temperature interval (283.15 to 323.15) K and at selected pressures between (0.1 and 60) MPa was reported. In this work, density measurements of these liquids (and toluene) in the same temperature and pressure intervals were made. Our objective was to analyze the potentiality of the combination of the isobaric heat capacity measurements with these density data to derive the complete set of properties. The specific calculation procedure is based on the derivation of α_p and κ_T from density data and on using the appropriate thermodynamic relations. The accuracy of this methodology was analyzed by the comparison with selected data from the literature. Moreover, its ability to describe both the temperature and pressure dependences of these properties was evaluated.

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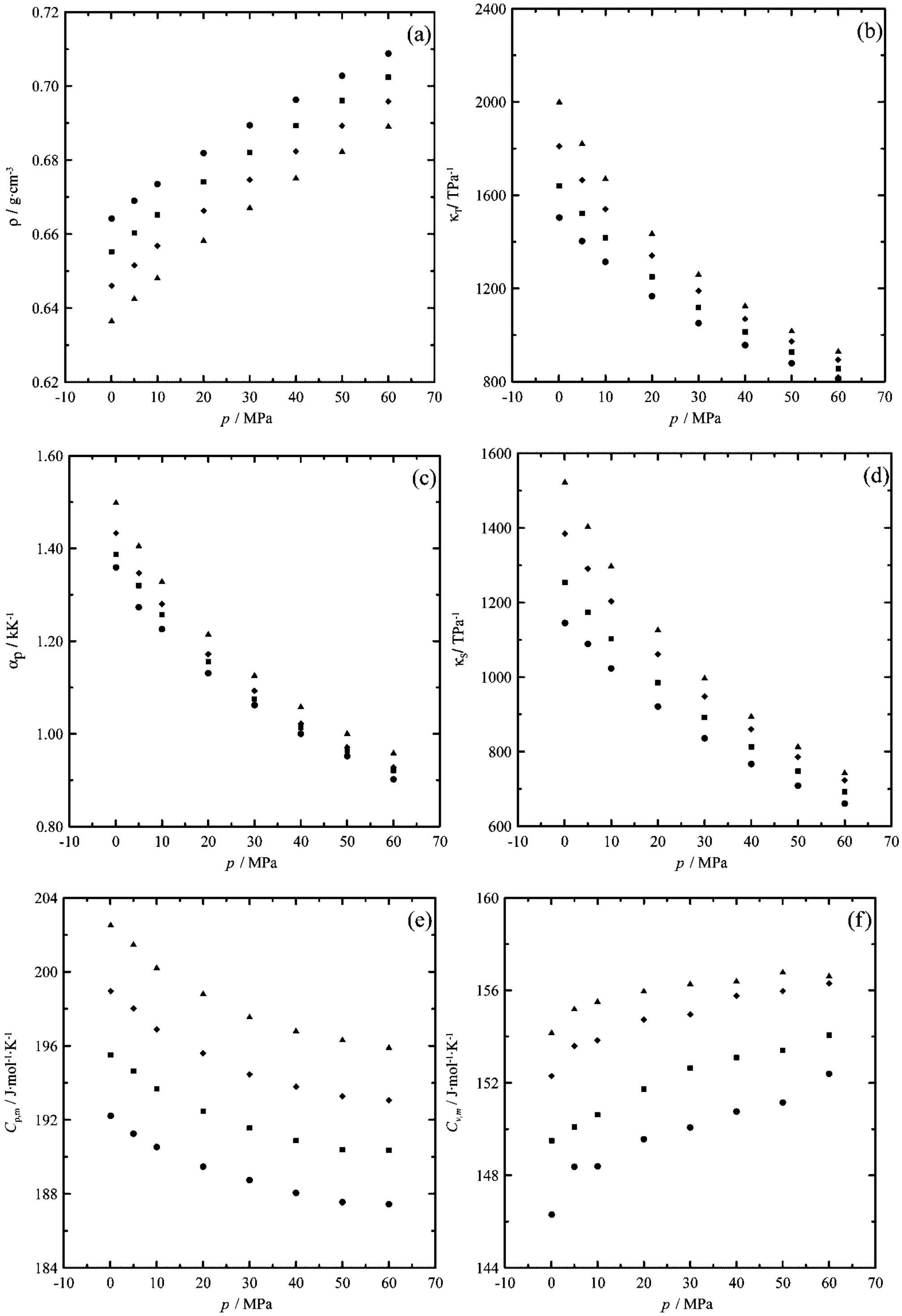

Figure 1. (a) Density, ρ, (b) isothermal compressibility, κ_T, (c) isobaric thermal expansivity, α_p, (d) isoentropic compressibility, κ_S, (e) isobaric molar heat capacity, $C_{p,\mathrm{m}}$, and (f) isochoric molar heat capacity, $C_{v,\mathrm{m}}$, of hexane plotted against pressure, p. ●, 288.15 K; ■, 298.15 K; ◆, 308.15 K; ▲, 318.15 K.

Materials and Equipment

Hexane (purity > 99.5 %), octane (purity > 99.5 %), and toluene (purity > 99.8 %) were purchased from Fluka, and nonane (purity > 99 %), decane (purity > 99.9 %), undecane (purity > 99 %), dodecane (purity > 99 %), tridecane (purity > 99 %), tetradecane (purity > 99 %), and 1-hexanol (purity 99 %) were purchased from Aldrich. Milli-Q water was obtained from the biochemistry laboratory of the University of Vigo. All chemicals were degassed prior to use; except water, all liquids were dried using molecular sieves of 0.4 nm.

Density was determined using automated equipment composed of a vibrating tube densimeter Anton Paar 512P, a model 7610 Ruska pressure controller, a Polyscience thermostatic bath, and a computer. The technical details of the apparatus can be found elsewhere.[10] The working equation for the determination of the density, ρ, of a sample using this equipment is given by the following expression

$$\rho = A + B\tau^2 \tag{1}$$

where A and B are calibration constants and τ is the oscillation period of the vibrating tube, which is the directly measured magnitude. Calibration constants were obtained using the classical calibration with two liquids of well-known density; we used octane and water taken the literature values from

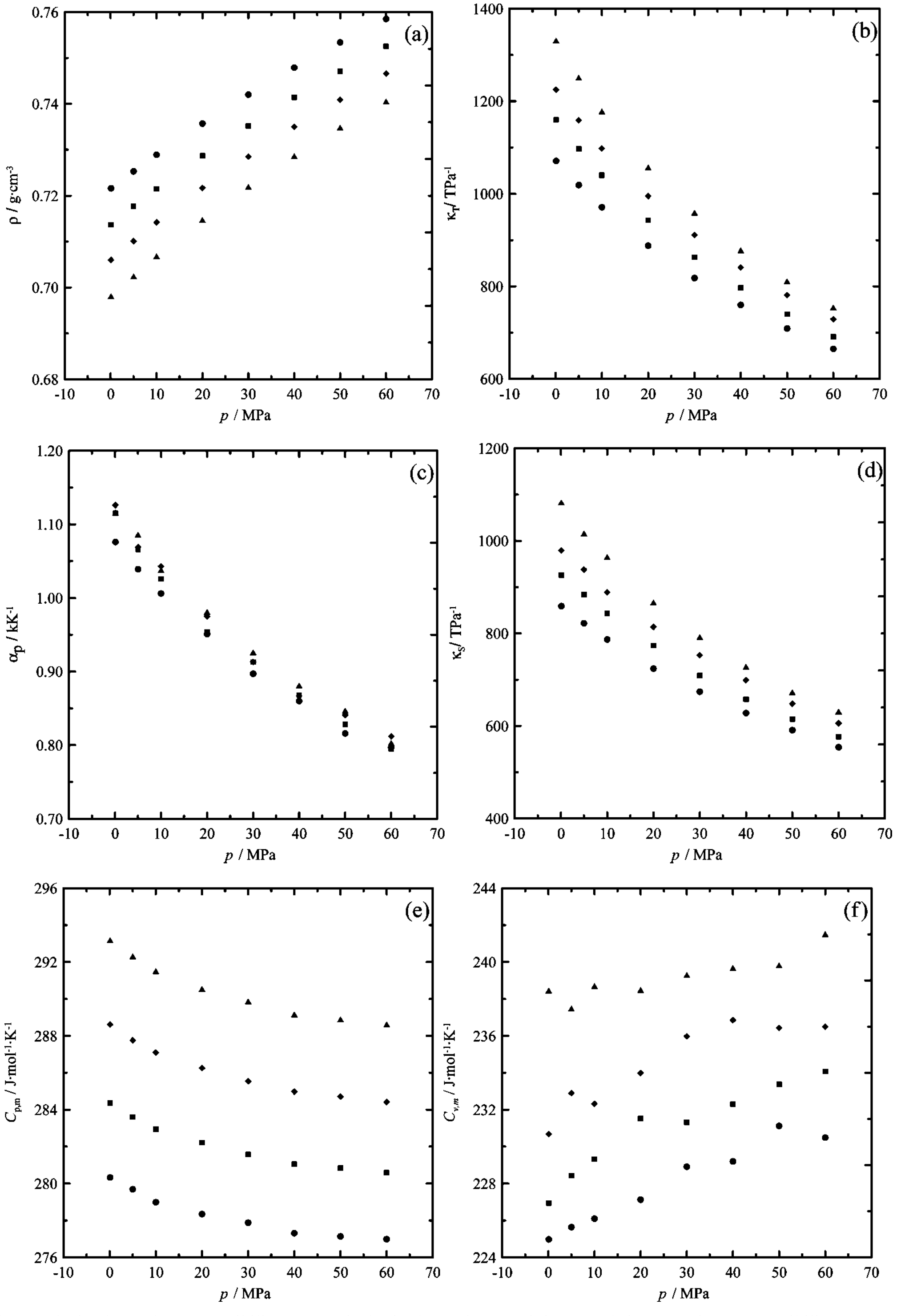

Figure 2. (a) Density, ρ, (b) isothermal compressibility, κ_T, (c) isobaric thermal expansivity α_p, (d) isoentropic compressibility, κ_S, (e) isobaric molar heat capacity, $C_{p,\mathrm{m}}$, and (f) isochoric molar heat capacity, $C_{v,\mathrm{m}}$, of nonane plotted against pressure, p. ●, 288.15 K; ■, 298.15 K; ◆, 308.15 K; ▲, 318.15 K.

Cibulka et al.[11,12] and Kell et al.,[13] respectively. These values were reported over the whole temperature and pressure intervals with uncertainty in the range of (0.00010 to 0.00020) $\mathrm{g \cdot cm^{-3}}$ for octane and (0.00001 to 0.00003) $\mathrm{g \cdot cm^{-3}}$ for water. Repeatability in the period, τ, during measurements was 0.00001 ms.

Results and Discussion

Density. The experimental values of density for all liquids are given in Tables A.1, A.2, A.3, A.4, A.5, A.6, A.7, A.8, and A.9 in the Supporting Information. These data for all liquids except toluene (for which there are no isobaric molar heat capacity data that allow the calculation of some of the other studied magnitudes) are also shown in Figures 1a, 2a, 3a, 4a, 5a, 6a, 7a, and 8a. The uncertainty $\sigma(\rho)$ of the density measurement of a liquid at temperature, T, and pressure, p, was calculated using method A. (See the Appendix.) It was found that, as a rule, $\sigma(\rho)$ depends on the considered pressure (atmospheric or higher pressure) and on the sample density. (It has no dependence on T.) At atmospheric pressure and for sample density values between (0.7 and 1) $\mathrm{g \cdot cm^{-3}}$, $\sigma(\rho)$ linearly varies from (0.0002 to 0.0001) $\mathrm{g \cdot cm^{-3}}$. At higher pressures, it varies from (0.0003 to 0.0002) $\mathrm{g \cdot cm^{-3}}$. We decided to give a

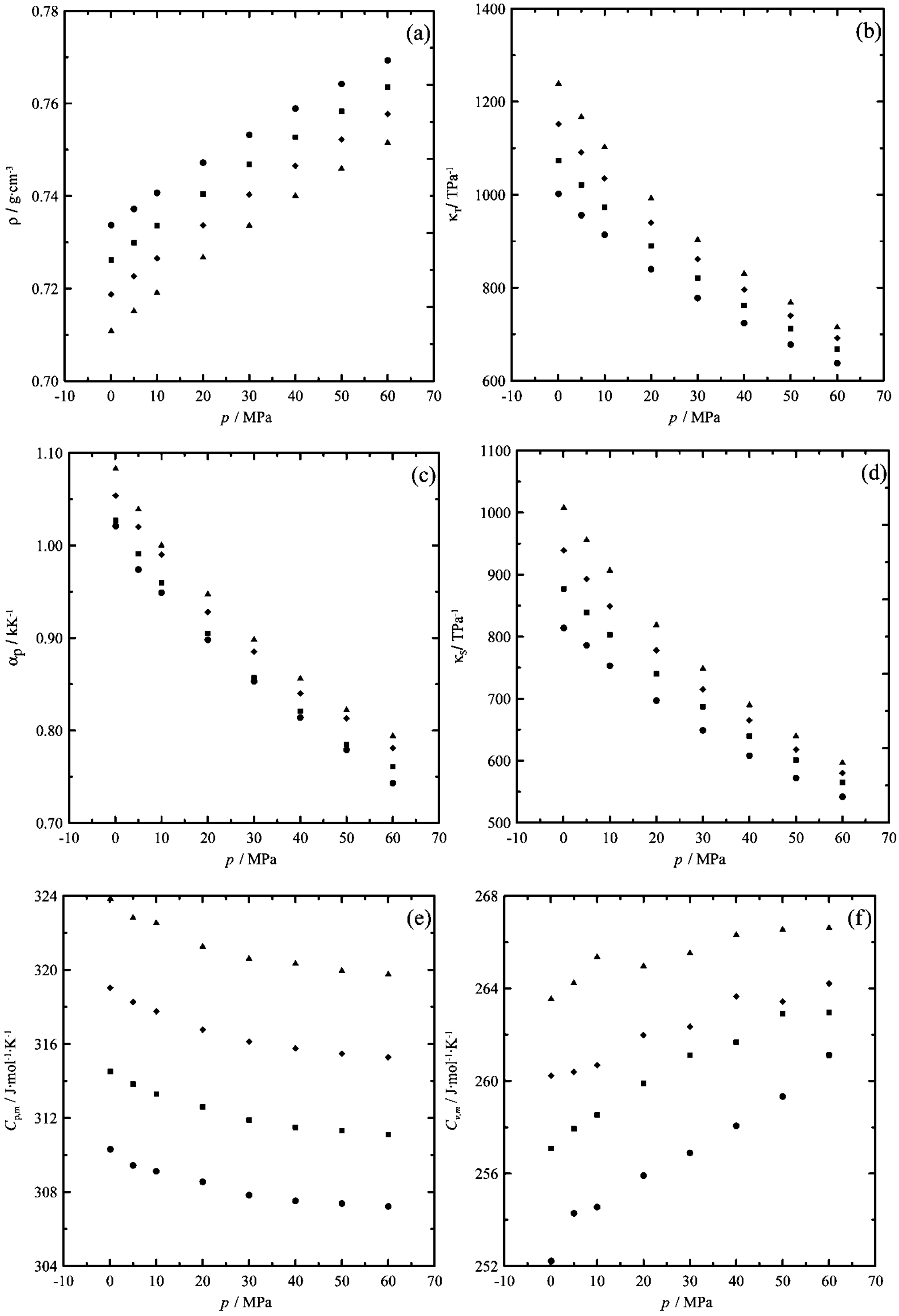

Figure 3. (a) Density, ρ, (b) isothermal compressibility, κ_T, (c) isobaric thermal expansivity, α_p, (d) isentropic compressibility, κ_S, (e) isobaric molar heat capacity, $C_{p,\mathrm{m}}$, and (f) isochoric molar heat capacity, $C_{v,\mathrm{m}}$, of decane plotted against pressure, p. ●, 288.15 K; ■, 298.15 K; ◆, 308.15 K; ▲, 318.15 K.

unique value of 0.0002 g·cm^{-3} for atmospheric pressure and 0.0003 g·cm^{-3} for higher pressures, which cover all of the measurements of this work. A comparison with selected data of the literature was done. At atmospheric pressure, data were taken from Cibulka et al. compilations,[11,14] which are given with an uncertainty of less than 0.00010 g·cm^{-3}. The deviations plotted in Figure 9 are consistent with the uncertainty of our measurements. (Only a few points surpass the value of 0.00030 g·cm^{-3}, which is the sum of the uncertainty of our data and that of the literature.) At higher pressures, a comparison was made for only hexane, nonane, decane, and toluene because their literature data (given by Cibulka et al.[11,12,14] correlations) are the most precise of the liquids studied in this work. The uncertainty of these data is not explicitly given, although it is not expected to be better than 0.00030 g·cm^{-3}. As can be seen in Figure 10, the agreement is good, and it validates our estimation of the uncertainty. (Deviations are never higher than 0.00060 g·cm^{-3}.)

Isothermal Compressibility. κ_T can be easily obtained from density data as a function of pressure, p, by means of its definition

$$\kappa_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T \tag{2}$$

Therefore, to obtain κ_T, the calculation of the derivative of the density with respect to pressure is needed. Theoretical considerations[15] have shown that the behavior of the density against pressure follows the behavior dictated by the Tait equation.[16] In that sense, the appropriate procedure to derive κ_T is to fit the density data at each temperature to the Tait equation

$$\rho(p) = \frac{\rho(0.1\ \mathrm{MPa})}{1 - C\ln\left(\dfrac{B + p}{B + 0.1\ \mathrm{MPa}}\right)} \tag{3}$$

and to obtain κ_T from these correlations. The fitting coefficients are the C and B parameters. This procedure was used for all liquids of this work, and κ_T data are given in Tables B.1, B.2, B.3, B.4, B.5, B.6, B.7, B.8, and B.9 of the Supporting Information. The experimental data, again for all liquids except

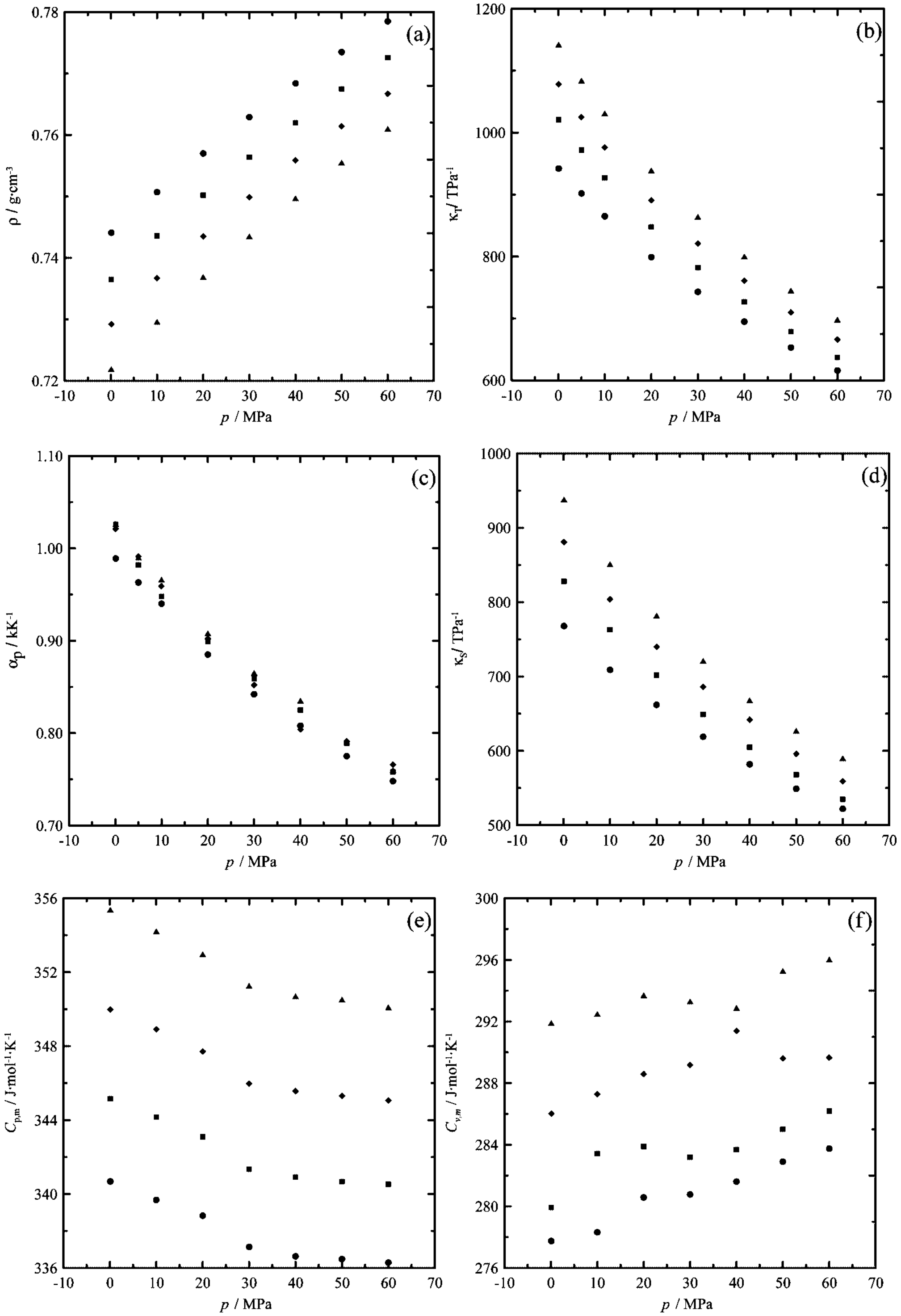

Figure 4. (a) Density, ρ, (b) isothermal compressibility, κ_T, (c) isobaric thermal expansivity, α_p, (d) isoentropic compressibility, κ_S, (e) isobaric molar heat capacity, $C_{p,\mathrm{m}}$, and (f) isochoric molar heat capacity, $C_{v,\mathrm{m}}$, of undecane plotted against pressure, p. ●, 288.15 K; ■, 298.15 K; ◆, 308.15 K; ▲, 318.15 K.

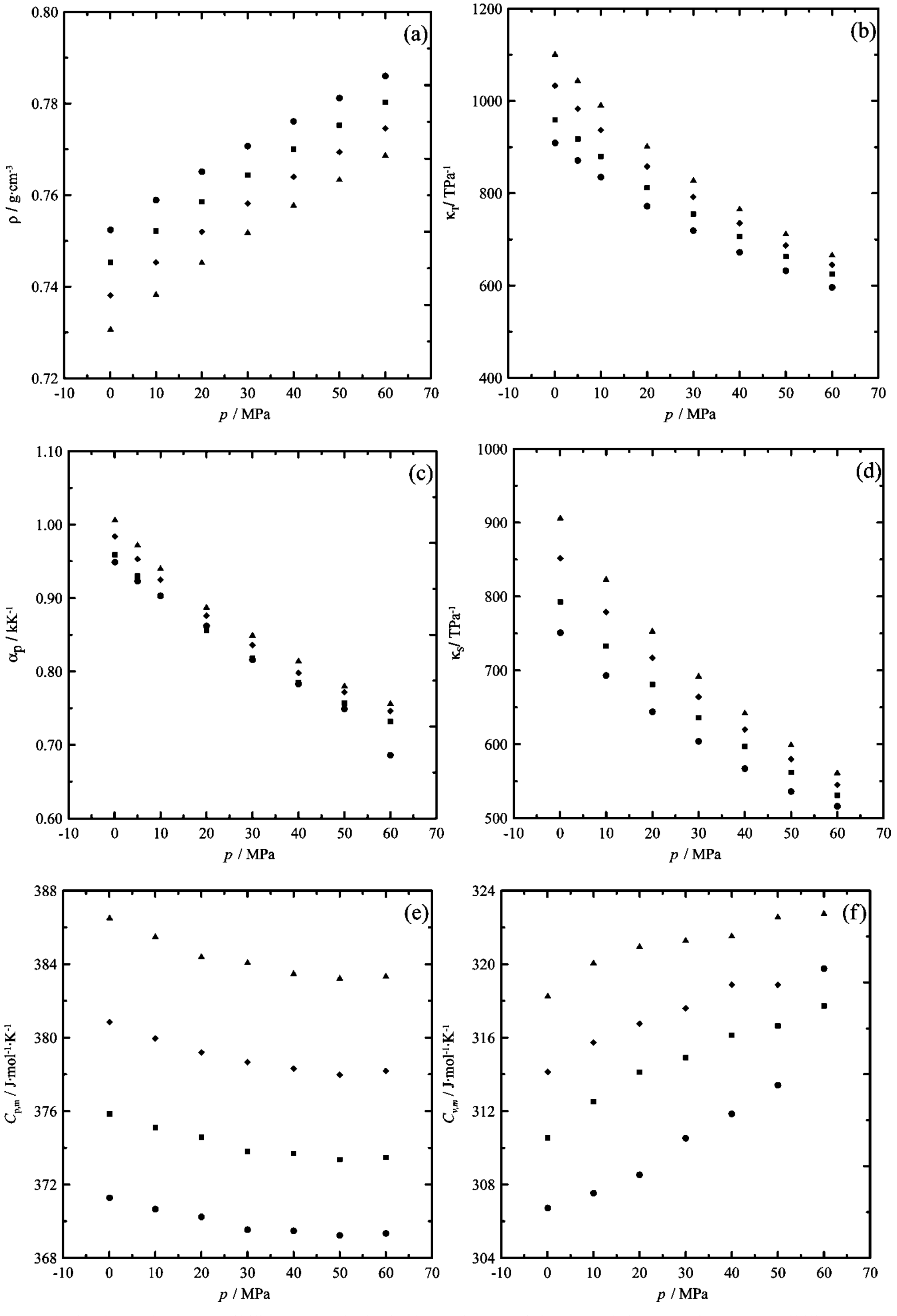

Figure 5. (a) Density, ρ, (b) isothermal compressibility, κ_T, (c) isobaric thermal expansivity, α_p, (d) isentropic compressibility, κ_S, (e) isobaric molar heat capacity, $C_{p,\mathrm{m}}$, and (f) isochoric molar heat capacity, $C_{v,\mathrm{m}}$, of dodecane plotted against pressure, p. ●, 288.15 K; ■, 298.15 K; ◆, 308.15 K; ▲, 318.15 K.

toluene, are represented in Figures 1b, 2b, 3b, 4b, 5b, 6b, 7b, and 8b.

The uncertainty in κ_T was estimated using method A described in the Appendix. Comparing the percent relative uncertainty $(\sigma(\kappa_T)/(\kappa_T))100$ obtained for a specific liquid, we found that it strongly depends on the considered pressure. (It has no dependence on T.) At the ends of the pressure interval ((0.1 and 60) MPa), the relative uncertainty is higher, and it continuously decreases from the ends to the intermediate pressures. This fact comes from the calculation of the derivative in eq 2, which is more accurate if a large number of experimental points were determined around the selected pressure. The relative uncertainty also depends on the density of the considered liquid; it increases from liquids with densities similar to water density to those with densities similar to that of octane, although this tendency is much milder than that found for pressure. The analysis of the uncertainty behavior gave a value of about 3 % for low pressure, it decreases to 0.8 % for intermediate pressures, and finally it increases to 2.5 % for the highest pressures.

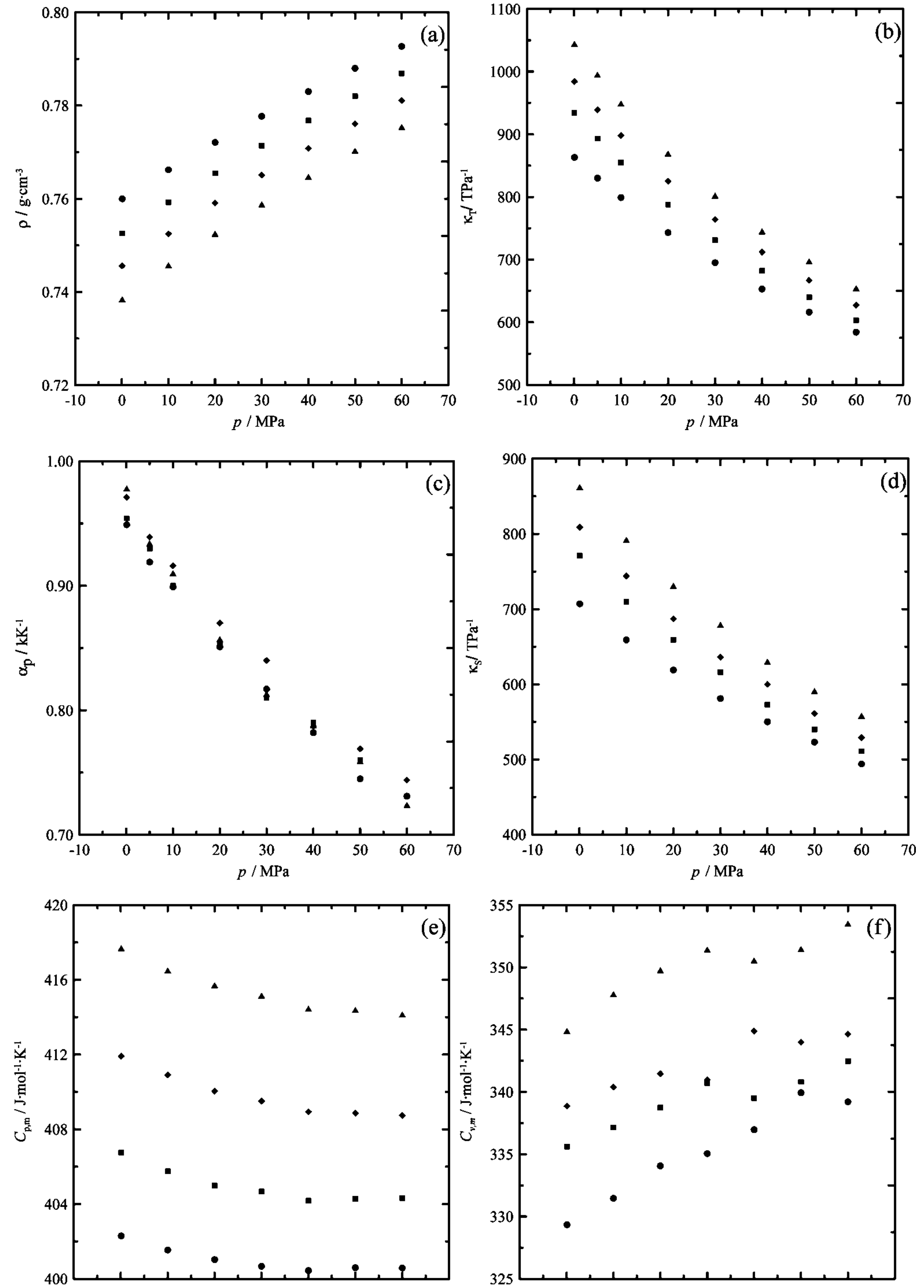

Figure 6. (a) Density, ρ, (b) isothermal compressibility, κ_T, (c) isobaric thermal expansivity, α_p, (d) isoentropic compressibility, κ_S, (e) isobaric molar heat capacity, $C_{p,\mathrm{m}}$, and (f) isochoric molar heat capacity, $C_{v,\mathrm{m}}$, of tridecane plotted against pressure, p. ●, 288.15 K; ■, 298.15 K; ◆, 308.15 K; ▲, 318.15 K.

Results for κ_T at atmospheric pressure are compared with selected literature data in Table 1, which were obtained from three different methods: data from refs 11, 12, and 14 were derived from Cibulka parametrizations; data from refs 17, 18, 19, 20, and 21 were directly determined with a relative uncertainty of 0.5 % using a piezometric technique; and data from refs 22 and 23 were obtained with an uncertainty of 1 TPa^{-1} from density, speed of sound, and isobaric heat capacity data using an adequate thermodynamic relation. As can be seen, deviations are in agreement with the estimated uncertainty. At higher pressures, the comparison of the obtained data and those from literature[11,12,14] showed that deviations follow the same pattern as the estimated uncertainty; the only discrepancy point is at the highest pressures, where deviations are normally lower than the estimated uncertainty. These results are presented in Figure S1 of the Supporting Information.

Isobaric Thermal Expansivity. This magnitude is defined from density, ρ, as follows

$$\alpha_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \qquad (4)$$

In this case, there is no general law giving the behavior of density with temperature that could yield a reliable equation such as the Tait equation (eq 3). A common procedure is to fit the density data to a polynomial and then derive α_p. However, this method has the important shortcoming of inducing a concrete dependency of α_p against T, which could be wrong in some cases. (For more details, see ref 22.) One appealing solution is to use the so-called incremental method, which is based on the following expression

$$\alpha_p(T_0) = \frac{1}{\rho(T_0)}\left(\frac{\rho(T_0 - \Delta T/2) - \rho(T_0 + \Delta T/2)}{\Delta T}\right) \qquad (5)$$

where ΔT is a temperature increment around T_0. This method is valid when the density behaves linearly in the interval ($T_0 - \Delta T/2$, $T_0 + \Delta T/2$); in a previous paper,[22] it was shown that $\Delta T = 10$ K is a good choice for a variety of liquids. This method was used for all liquids of this work, and results are given in Tables C.1, C.2, C.3, C.4, C.5, C.6, C.7, C.8, and C.9 in the Supporting Information. These data are shown in Figures 1c, 2c, 3c, 4c, 5c, 6c, 7c, and 8c (except for toluene).

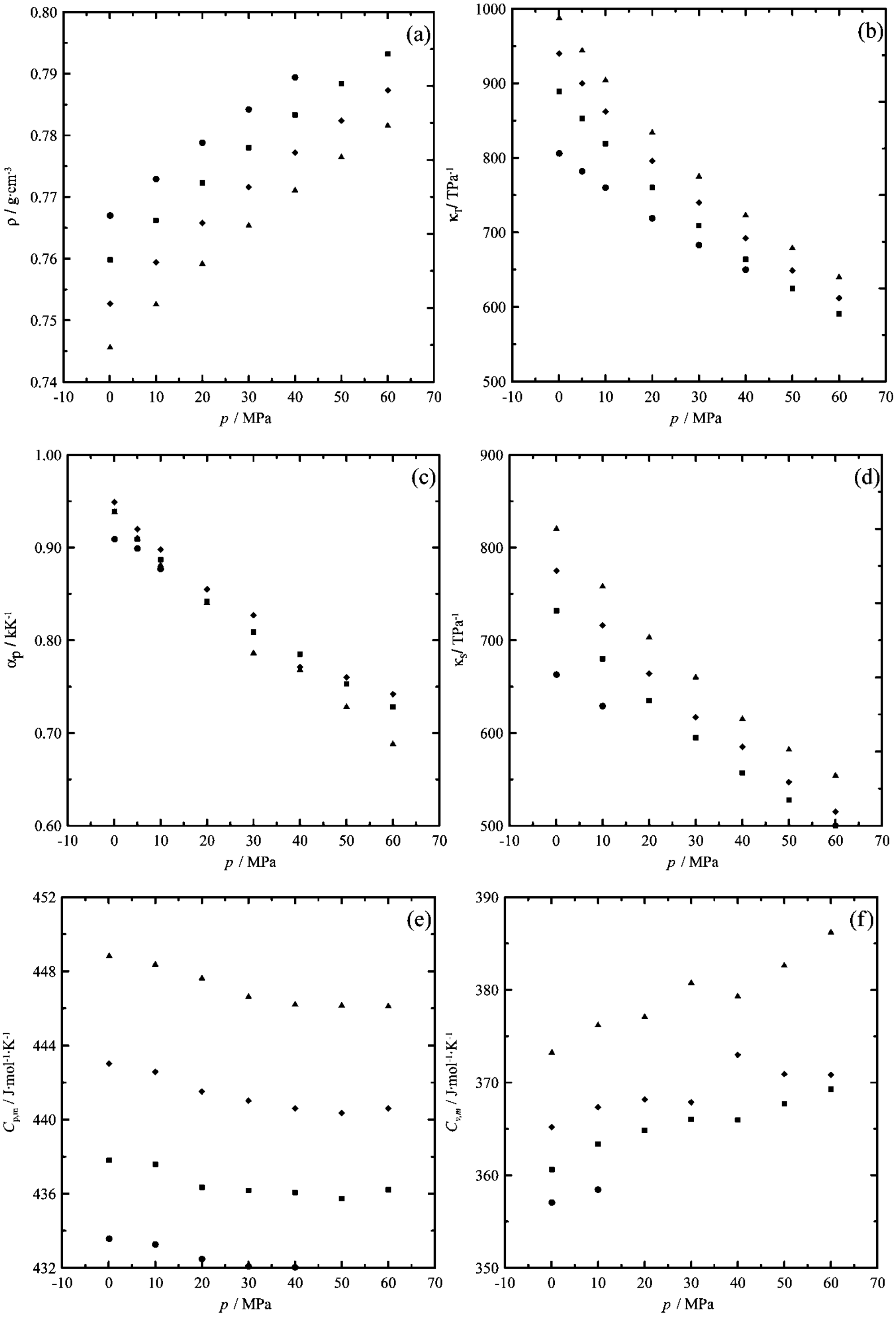

Figure 7. (a) Density, ρ, (b) isothermal compressibility, κ_T, (c) isobaric thermal expansivity, α_p, (d) isentropic compressibility, κ_S, (e) isobaric molar heat capacity, $C_{p,\mathrm{m}}$, and (f) isochoric molar heat capacity, $C_{v,\mathrm{m}}$, of tetradecane plotted against pressure, p. ●, 288.15 K; ■, 298.15 K; ◆, 308.15 K; ▲, 318.15 K. There are missing data at 288.15 K and high pressure because of the freezing of tetradecane.

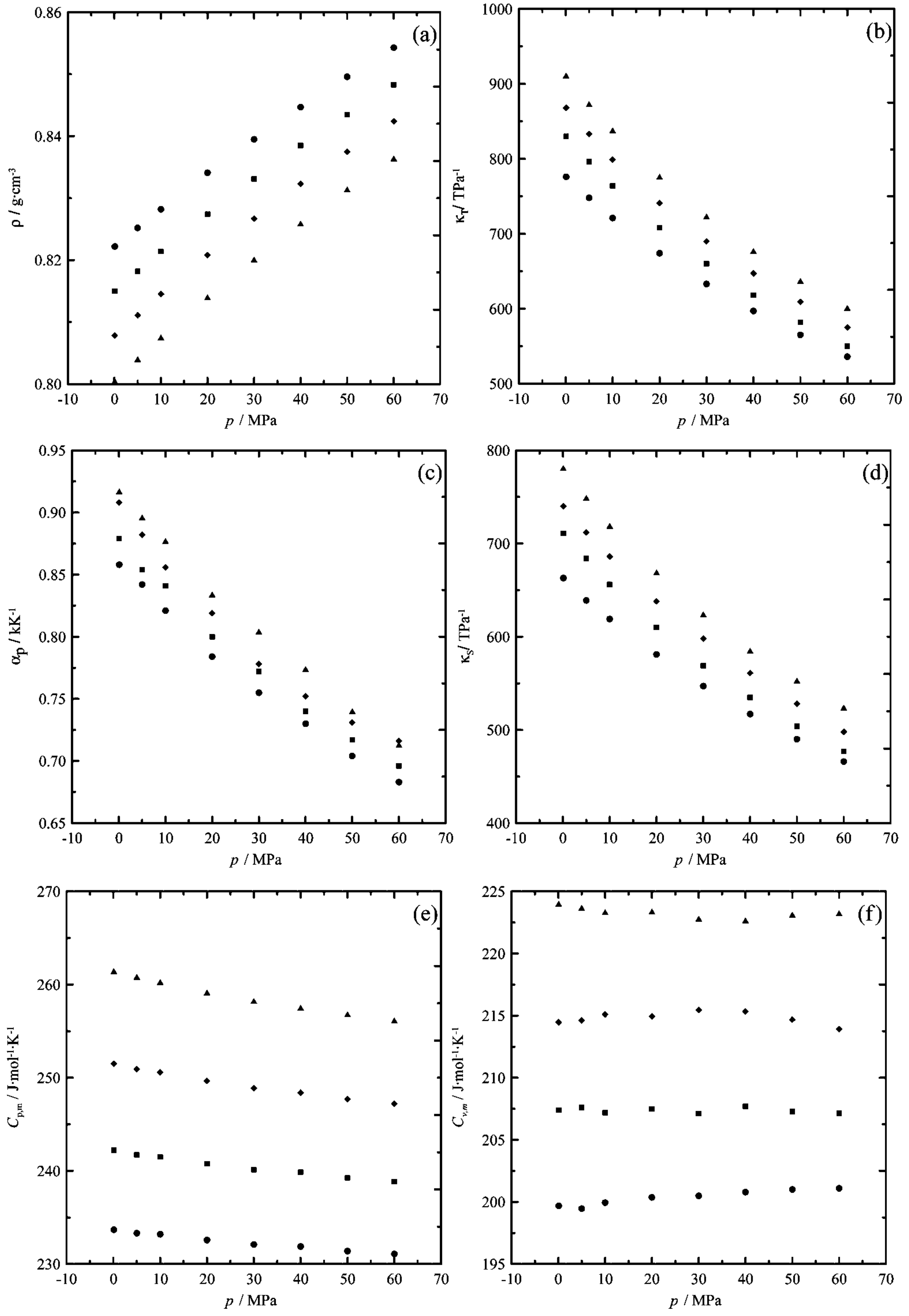

Figure 8. (a) Density, ρ, (b) isothermal compressibility, κ_T, (c) isobaric thermal expansivity, α_p, (d) isoentropic compressibility, κ_S, (e) isobaric molar heat capacity, $C_{p,\mathrm{m}}$, and (f) isochoric molar heat capacity, $C_{v,\mathrm{m}}$, of 1-hexanol plotted against pressure, p. ●, 288.15 K; ■, 298.15 K; ◆, 308.15 K; ▲, 318.15 K.

The uncertainty $\sigma(\alpha_p)$ was calculated using method A, and it takes an approximately constant value for all liquids: 0.030 kK^{-1} at atmospheric pressure and 0.050 kK^{-1} for higher pressures. In Table 2, results of this work at atmospheric pressure are compared with literature data. They were taken from the recommended values in Timmermans[24] and Riddick[25] compilations from refs 22, 23, 26, 27, and 28, which were obtained with an uncertainty of 0.003 kK^{-1}, and some of them were calculated from the Cibulka correlations.[11,14] As can be seen, good agreement between both sets of data is found; in all cases, deviations never exceed 0.017 kK^{-1}, which suggests that our uncertainty estimation was wrong. This overestimation also appears at higher pressures, where comparison was done using the data of Cibulka et al.[11,12,14] The average deviation was 0.020 kK^{-1}, and only a few points surpassed 0.030 kK^{-1}. (See Figure S2 in the Supporting Information.) This fact was also observed in a previous work,[22] and it can be ascribed to the cancellation of systematic errors in the calculation of α_p using eq 5. Taking into account these results, we decided to give the values of (0.015 and 0.030) kK^{-1} for the uncertainty of α_p at atmospheric and higher pressures, respectively.

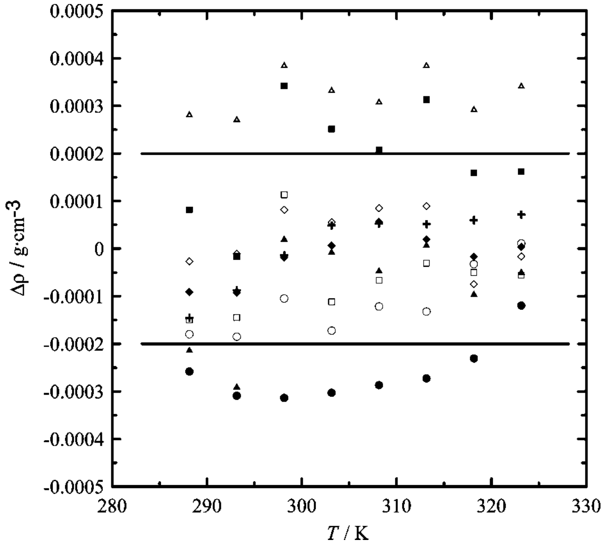

Figure 9. Deviation, $\Delta\rho$, between densities of this work and literature ones at atmospheric pressure plotted against temperature, T, for ●, hexane; ■, nonane; ◆, decane; ▲, undecane; +, dodecane; ○, tridecane; □, tetradecane; ◇, toluene; △, 1-hexanol. —, Uncertainty.

Isentropic Compressibility. κ_S was obtained from ρ and $C_{p,\mathrm{m}}$ data and the derived properties α_p and κ_T using the next thermodynamic relation

$$\kappa_S = \kappa_T - \frac{TP_\mathrm{m}\alpha_p^2}{\rho C_{p,\mathrm{m}}} \qquad (6)$$

where P_m is the molecular weight. Results for κ_S are given in Tables D.1, D.2, D.3, D.4, D.5, D.6, D.7, and D.8 in the Supporting Information, and they are shown in Figures 1d, 2d, 3d, 4d, 5d, 6d, 7d, and 8d (except toluene). The $C_{p,\mathrm{m}}$ data for the studied liquids (except toluene, for which there are no available $C_{p,\mathrm{m}}$ literature data) were obtained from ref 9, and they are shown in Figures 1e, 2e, 3e, 4e, 5e, 6e, 7e, and 8e. Uncertainty in κ_S was not estimated using method A because α_p is involved in the calculations and, as explained in the last paragraph, its uncertainty was not obtained from the method A. With this view, $\sigma(\kappa_S)$ was estimated using the common uncertainty estimation technique (method B in the Appendix). The $\sigma(\kappa_S)$ calculation was performed using eq 6, the corresponding values of α_p, ρ, C_p, and κ_T, and their uncertainties. Comparing all of the percent relative uncertainties $(\sigma(\kappa_S)/(\kappa_S))100$, we found that $(\sigma(\kappa_S)/(\kappa_S))100$ follows the same behavior as the relative uncertainty of κ_T; at low pressure, it is estimated to be about 5 %, it decreases to 2 % for intermediate pressures, and it increases to 4 % for the higher pressures. (See Figure S3 in the Supporting Information.) The comparison with literature selected data at atmospheric pressure is given in Table 3. These values were taken from the recommended values in Riddick[25] compilation and those from references;[22,23,26–28] the latter were determined with a precision of 0.15 TPa^{-1} from density and speed of sound measure-

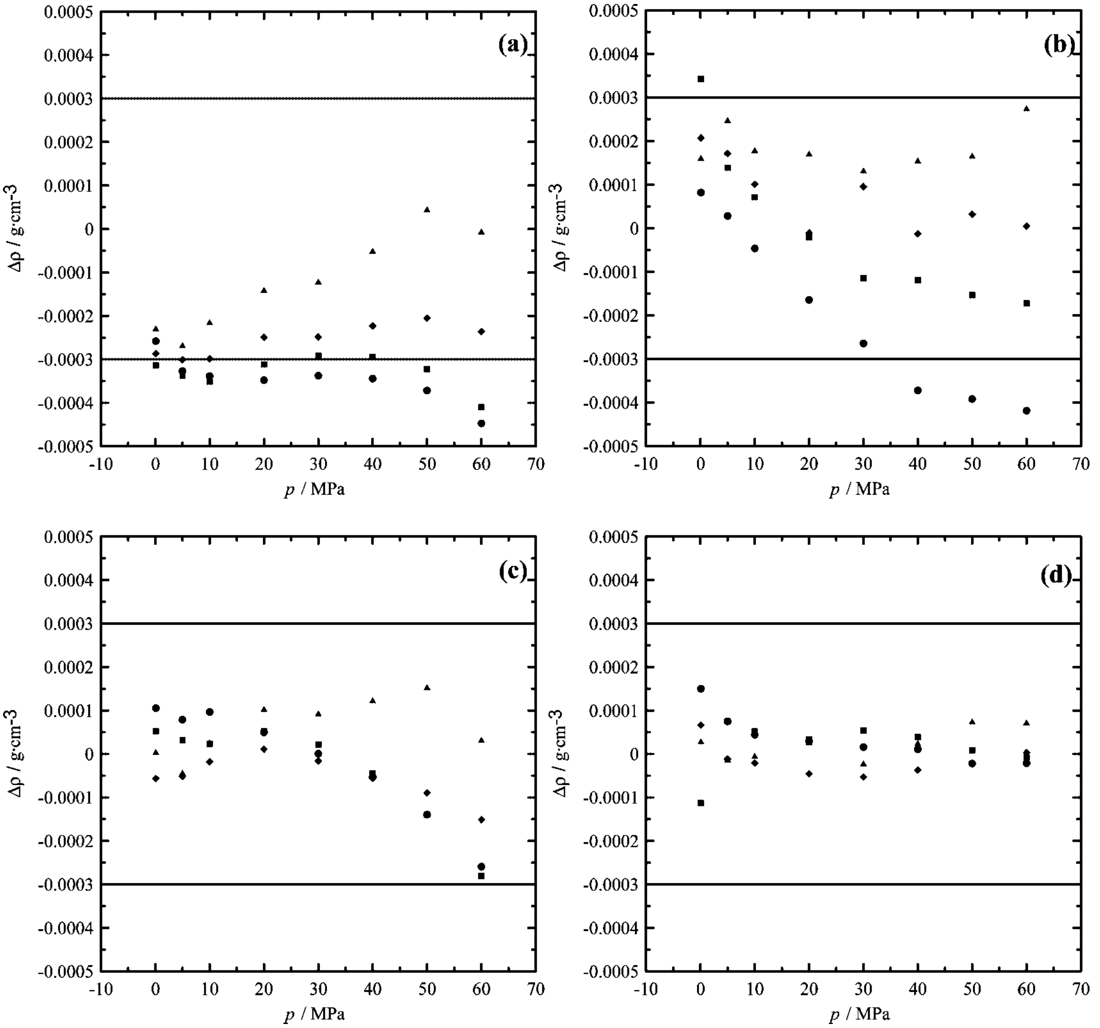

Figure 10. Deviation $\Delta\rho$ between densities of this work and literature ones plotted against pressure, p, for (a) hexane, (b) nonane, (c) decane, and (d) toluene. ●, 288.15 K; ■, 298.15 K; ◆, 308.15 K; ▲, 318.15 K. —, Uncertainty.

Table 1. Isothermal Compressibility, κ_T, of This Work and Literature Data for Several Liquids at Atmospheric Pressure and at the Temperature, T^a

	T	κ_T/TPa^{-1}		$\Delta\kappa_T$	PRD
liquid	K	this work	literature	TPa^{-1}	%
hexane	293.15	1566	1618[22]	−52	3.3
	298.15	1640	1644[11,12]	−4	0.2
	303.15	1721	1784[22]	−63	3.7
	308.15	1810	1844[17]	−34	1.9
	313.15	1904	1973[22]	−69	3.6
	318.15	2002	2033[17]	−31	1.5
	323.15	2108	2191[22]	−83	3.9
nonane	298.15	1160	1177[17]	−17	1.5
decane	298.15	1073	1081[11,12]	−8	0.7
undecane	323.15	1188	1208[11,12]	−20	1.7
dodecane	283.15	886	897[23]	−11	1.2
	293.15	934	959[23]	−25	2.7
	298.15	959	987[19]	−28	2.9
	303.15	996	1027[23]	−31	3.1
	308.15	1033	1052[19]	−19	1.8
	313.15	1063	1100[23]	−37	3.5
	318.15	1102	1127[19]	−25	2.3
	323.15	1137	1179[23]	−42	3.7
tridecane	298.15	934	944[20]	−10	1.1
tetradecane	298.15	889	910[21]	−21	2.4
toluene	303.15	940	933[14]	7	0.7
1-hexanol	298.15	830	836[18]	6	0.7

[a] $\Delta\kappa_T$ and PRD are the deviation and the percent relative deviation, respectively, between both sets of data.

Table 2. Isobaric Thermal Expansivity, α_p, of This Work and Literature Data for Several Liquids at Atmospheric Pressure and at Temperature, T^a

	T	α_p/kK^{-1}		$\Delta\alpha_p$	PRD
liquid	K	this work	literature	kK^{-1}	%
hexane	293.15	1.358	1.361[22]	−0.003	0.2
	298.15	1.387	1.387[11]	0.000	0.0
	313.15	1.461	1.452[24]	0.009	0.6
nonane	288.15	1.075	1.069[11]	0.006	0.6
decane	298.15	1.027	1.039[26]	−0.012	1.2
undecane	308.15	1.015	1.013[11]	0.002	0.0
dodecane	288.15	0.948	0.956[22]	−0.008	0.8
	293.15	0.953	0.964[23]	−0.011	1.2
	298.15	0.959	0.968[27]	−0.009	0.9
	303.15	0.974	0.978[23]	−0.004	0.4
	313.15	0.990	0.992[23]	−0.002	0.2
tridecane	298.15	0.963	0.950[25]	0.013	1.3
tetradecane	298.15	0.948	0.931[28]	0.017	1.8
1-hexanol	298.15	0.887	0.878[25]	0.009	1.0
toluene	298.15	1.076	1.080[14]	−0.004	0.4

[a] $\Delta\alpha_p$ and PRD are the deviation and the percent relative deviation, respectively, between both sets of data.

Table 3. Isoentropic Compressibility, κ_S, of This Work and Literature Data for Several Liquids at Atmospheric Pressure and at 298.15 K^a

	κ_S/TPa^{-1}		$\Delta\kappa_S$	PRD
liquid	this work	literature	TPa^{-1}	%
hexane	1254	1317[22]	−63	5.0
decane	877	904[26]	−27	3.1
dodecane	792	821[23]	−29	3.6
tridecane	767	791[27]	−24	3.1
tetradecane	729	765[28]	−36	4.8
1-hexanol	709	722[25]	−13	1.8

[a] $\Delta\kappa_S$ and PRD are the deviation and the percent relative deviation, respectively, between both sets of data.

ments using the Laplace equation. At higher pressures, the comparison was made against data obtained from Daridon et al.[29] and Kasashaian et al.,[30] who estimated an uncertainty for their measurements of 0.1 % (Figure S3 in the Supporting Information). The deviations are consistent with the previously estimated uncertainty and that of the literature data. Moreover, as a general rule, deviations follow the behavior against pressure of the estimated uncertainty.

Table 4. Isochoric Molar Heat Capacity, $C_{v,m}$, of this Work and Literature Data for Several Liquids at Atmospheric Pressure and at 298.15 K^a

	$C_{v,m}$/J·mol^{-1}·K^{-1}		$\Delta C_{v,m}$	PRD
liquid	this work	literature	J·mol^{-1}·K^{-1}	%
hexane	149.51	151.00[25]	−1.49	1.0
decane	257.09	257.30[26]	−0.21	0.1
dodecane	310.49	310.50[31]	−0.01	0.0
tridecane	334.25	338.40[28]	−4.15	1.2
tetradecane	359.11	365.29[31]	−6.18	1. 7

[a] $\Delta C_{v,m}$ and PRD are the deviation and the percent relative deviation, respectively, between both sets of data.

Isochoric Molar Heat Capacity. This magnitude was calculated from ρ and $C_{p,m}$ data and the derived properties α_p and κ_T using the next thermodynamic relation

$$C_{v,m} = C_{p,m} - \frac{TP_m\alpha_p^2}{\rho\kappa_T} \tag{7}$$

Results for $C_{v,m}$ are given in Tables E.1, E.2, E.3, E.4, E.5, E.6, E.7, and E.8 in the Supporting Information and are represented in Figures 1f, 2f, 3f, 4f, 5f, 6f, 7f, and 8f. As for κ_S, α_p is needed for obtaining $C_{v,m}$; therefore, uncertainty, $\sigma(C_{v,m})$, was estimated using method B described in the Appendix. For each $\sigma(C_{v,m})$ determination, the corresponding values of α_p, ρ, C_p, and κ_T and their previously defined uncertainties were used. Comparing the relative uncertainties $(\sigma(C_{v,m})/(C_{v,m}))100$, we found that it slightly depends on pressure but is independent of the sample density and temperature. With this view, we have decided to give a unique value of 1.5 %. To check the correctness of this uncertainty estimation, comparisons were made at both atmospheric and higher pressures. At atmospheric pressure, literature data were taken from the recommended values in Riddick compilation[25] and from references;[26,28,31] the latter were determined with a precision of 0.25 J·mol^{-1}·K^{-1} from density, speed of sound, and isobaric heat capacity measurements using common thermodynamic relations. At higher pressures, data for hexane were taken from Randzio et al.,[7] which were obtained from calorimetric determination of the isobaric thermal expansivity as a function of pressure (method iv described in the introduction). We determined data for tridecane[8] by using a procedure similar to that of this work, giving an uncertainty of 2.5 %. As can be seen, deviations observed in Table 4 and Figure S4 of the Supporting Information confirm our estimation of uncertainty.

Global Performance of the Methodology. Figures 1, 2, 3, 4, 5, 6, 7, and 8 show the complete set of magnitudes as a function of pressure for several isotherms of all studied liquids (except toluene). As can be seen, this experimental methodology is accurate enough to describe the pressure and temperature dependences of all of these properties in the working interval. However, the degree of accuracy is different for each one; specifically, the isochoric molar heat capacity and isoentropic compressibility are the least accurate magnitudes, which comes from the fact that they are derived from not only the directly measured properties, ρ and $C_{p,m}$, but also the derived ones, κ_T and α_p. Undoubtedly, κ_S, can be more accurately determined from the speed of sound and density measurements at both atmospheric and higher pressures, but as for $C_{v,m}$ at high pressure, the precision is similar to that obtained from other methodologies. The more accurate data were given by Bessieres et al.,[8] with a precision of 2.5 %, and Polikhronidi et al.,[32] who used a high pressure, high temperature, adiabatic, and nearly constant volume calorimeter to determine it directly with an accuracy of 2 %; both methodologies yield uncertainties similar (even a bit worse) than that obtained in this work (1.5 %).

Conclusions

The proposed method for obtaining isothermal and isoentropic compressibilities, isobaric thermal expansivity and isochoric molar heat capacity from density and isobaric molar heat capacity against temperature and pressure, has been revealed to be highly reliable, which makes it appropriate to be used for precise characterization of the behavior of liquids against temperature and pressure.

Appendix

Let a magnitude y, which is calculated from N different magnitudes $x_1, x_2,..., x_N$, by using an arbitrary expression $y = f(x_1, x_2,..., x_N)$. Let x_1^M,x_2^M,..., x_N^M, the result of an experimental measurement, $\sigma(x_1^M)$,$\sigma(x_2^M)$,...,$\sigma(x_N^M)$, their uncertainties, and y^M, the corresponding value of indirect magnitude y. The uncertainty of this measurement, $\sigma(y^M)$, was obtained from method A, if y is density, isothermal compressibility, isobaric thermal expansivity, or method B, in the other cases.

Method A consists of the next steps: (i) A set of N different values, x_1^1, x_2^1,..., x_N^1, are randomly estimated in the intervals $(x_1^M - \sigma(x_1^M), x_1^M + \sigma(x_1^M))$,$(x_2^M - \sigma(x_2^M), x_2^M + \sigma(x_2^M))$,..., $(x_N^M - \sigma(x_N^M), x_N^M + \sigma(x_N^M))$, respectively. From this set of values, the magnitude y^1 is calculated. (ii) Step i is repeated K times to collect K different values of the magnitude y, denoted as y^1,y^2,..., y^K. (iii) $\sigma(y^M)$ was chosen for the interval $(y^M - \sigma(y^M), y^M + \sigma(y^M))$ to contain 95 % of the K values of the y magnitude.

Method B is based on the common uncertainty propagation technique on the basis of the following expression

$$\sigma(y^M) = \sqrt{\sum_{i=1}^{N}\left(\frac{\partial y}{\partial x_i}\right)^2 \sigma^2(x_i^M)} \qquad \text{(A1)}$$

Supporting Information Available:

Experimental data for density, isothermal and isoentropic compressibilities, isobaric thermal expansivity, and isochoric molar heat capacity and their comparison with literature data for isothermal and isentropic compressibilities, isobaric thermal expansivity, and isochoric molar heat capacity. The behavior of the uncertainty of these properties against pressure is also included. This material is available free of charge via the Internet at http://pubs.acs.org.

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