*J. Chem. Eng. Data* **2010,** *55,* 2173–2179

# Isobaric Thermal Expansivity for Nonpolar Compounds

**Paloma Navia, Jacobo Troncoso, and Luís Romaní***

Departamento de Física Aplicada, Facultad de Ciencias de Ourense, Campus As Lagoas, 32004 Ourense, Spain

Isobaric thermal expansivity for a set of nonpolar compounds is determined in the temperature and pressure intervals of (278.15 to 348.15) K and (0.6 to 55) MPa using a calorimetric method. The selected compounds are benzene, tetrachloromethane, and the alkane series, from nonane to pentadecane. These results are compared with literature data, with most of them obtained from density measurements. Temperature behavior is revealed to be highly dependent on the experimental pressure; at low pressure, isobaric thermal expansivity clearly increases with temperature. This dependence becomes milder as pressure is raised, and for some liquids at high pressure, it is undoubtedly observed that $\alpha_p$ decreases against $T$. These results are rationalized by relating them with phase transition properties, concretely, vapor pressure and critical coordinates. Finally, well-known thermodynamic relations are used to obtain density and isobaric molar heat capacity as a function of temperature and pressure from isobaric thermal expansivity, density, and heat capacity at atmospheric pressure. The results thus obtained were compared with directly measured data.

## Introduction

Accurate experimental determination of second-order thermodynamic properties of liquids against temperature and pressure is of high interest for thermophysical sciences, since it allows characterizing their thermodynamic behavior, which, evidently, has important consequences from both a fundamental and an applied point of view. The most studied second-order thermodynamic properties are isobaric heat capacity, isentropic and isothermal compressibilities, and, to a lesser extent, isochoric heat capacity and isobaric thermal expansivity, a fact which is motivated by the accuracy and simplicity of the available experimental methodologies. Isobaric molar heat capacity is easily obtained with high accuracy using a variety of techniques;[1–3] this is not the case of isochoric heat capacities, since the constant volume constraint involves strong experimental complications, which worsen the accuracy of the methodology.[4] Precise isentropic compressibilities can be determined from accurate density and speed of sound measurements,[5–8] whereas isothermal compressibilities $\kappa_T$ are easily and accurately obtained from precise density measurements against pressure, by making use of the Tait equation.[9–12] By contrast, isobaric thermal expansivity $\alpha_p$ is not as accurately obtained as $\kappa_T$, although it could be thought that a similar procedure than that used with $\kappa_T$ could be used, that is, fitting precise density data against temperature to some equation. Nevertheless, there is no equation which can represent the behavior against temperature as well as Tait's one does against pressure. Alternative methods[9,13–24] have been proposed; among them, the most often used are those based on determining $\alpha_p$ from density measurements,[9,13,14] which requires high quality density data, not always available, especially at high pressure, and those grounded on the $\alpha_p$ determination from calorimetric measurements against pressure,[15–30] which have the advantage of obtaining $\alpha_p$ directly, without any prejudiced assumption about the dependence of density against temperature.

In this work, isobaric thermal expansivity for a set of nonpolar compounds is experimentally determined using a calorimetric technique in the temperature and pressure intervals of (278.15 to 348.15) K and (0.6 to 55) MPa. The selected compounds are benzene, tetrachloromethane, and the alkane series, from nonane to pentadecane. The results are compared with available literature data, with most of them obtained from density measurements. The strong dependence of $\alpha_p$ temperature behavior against pressure, already observed for other compounds,[15,17,18,20,23] which, in some cases, induces curve crossing at high pressure, is explained by paying attention to vapor pressure and critical properties of the liquids, because of the strong relation between $\alpha_p$ and fluctuations, which become very important in the proximity of the critical point. From $\alpha_p$ data and by means of well-known thermodynamic relations, it is possible to obtain density, $\rho$, as a function of temperature from $\rho$ at one temperature and $C_{p,\mathrm{m}}$ as a function of pressure from $C_{p,\mathrm{m}}$ at one pressure. This is done using $\alpha_p$ data from this work, and these calculations are compared with directly measured literature data, obtaining good results for most of studied liquids.

## Experimental Section

***Chemicals.*** Calibration of the apparatus required two standard liquids; Milli-Q water and hexane obtained from Fluka (with a mass fraction purity > 0.99) were used. Benzene (mass fraction purity > 0.998), tetrachloromethane (mass fraction purity > 0.99), nonane (mass fraction purity > 0.99), decane (mass fraction purity > 0.99), undecane (mass fraction purity > 0.99), dodecane (mass fraction purity > 0.99), tridecane (mass fraction purity > 0.99), tetradecane (mass fraction purity > 0.99), and pentadecane (mass fraction purity > 0.99) were purchased from Aldrich. All liquids were degassed and passed through molecular sieves to remove traces of water.

***Experimental Methodology.*** Isobaric thermal expansivity of the studied liquids was determined through a Micro DSCII microcalorimeter from Setaram coupled with a Ruska 7610 pressure controller (pressure regulation within ± 0.005 MPa).[16,31] The method for obtaining $\alpha_p$ is based on recording the heat exchange between the cell which contains the studied liquid

---

* Corresponding author. E-mail: romani@uvigo.es. Telephone: +34-988387213. Fax: +34-988387227.

10.1021/je900757k

and the calorimetric block because of the variation of the pressure over the sample; $\alpha_p$ was obtained from the next expression, derived from a Maxwell's relation:

$$\alpha_p = -\frac{1}{VT}\frac{\mathrm{d}'Q}{\mathrm{d}p} \tag{1}$$

where $V$ is the cell volume, and $\mathrm{d}'Q/\mathrm{d}p$ is the variation of the heat introduced in the sample against change in pressure. Once the sample was introduced in the experimental cell and thermal stability at the measuring temperature was reached (the uncertainty in temperature was estimated in ± 0.01 K), the pressure was varied using a pressure ramp at 1.5 $\mathrm{MPa \cdot min^{-1}}$. This introduced a heat flux $\phi^{\mathrm{x}}$ between the sample and the calorimetric block. For calibrating, two standard liquids were needed: water and hexane were selected because of the quality of the available literature data.[15,32] For determining the isobaric thermal expansivity of the sample, $\alpha_p{}^{\mathrm{x}}$, the fluxes for water and hexane, $\phi^{\mathrm{w}}$ and $\phi^{\mathrm{h}}$, obtained in two experiences at the same experimental conditions, were required. From these fluxes and from isobaric thermal expansivity for water and hexane, $\alpha_p{}^{\mathrm{w}}$ and $\alpha_p{}^{\mathrm{h}}$, the isobaric thermal expansivity of the unknown liquid was obtained from the measured flux $\phi^{\mathrm{x}}$, through:

$$\alpha_p^{\mathrm{x}} = \alpha_p^{\mathrm{w}} + \frac{\phi^{\mathrm{w}} - \phi^{\mathrm{x}}}{\phi^{\mathrm{w}} - \phi^{\mathrm{h}}}(\alpha_p^{\mathrm{h}} - \alpha_p^{\mathrm{w}}) \tag{2}$$

The repeatability of $\alpha_p$ was estimated in $0.005 \cdot 10^{-3}\ \mathrm{K^{-1}}$, which together with the uncertainty stated for the calibration fluids, yielded for $\alpha_p$ an uncertainty of 2 %.

## Results and Discussion

Isobaric thermal expansivity data were obtained in temperature and pressure steps of 10 K and 0.35 MPa, respectively, within the temperature and pressure intervals of (278.15 to 348.15) K and (0.6 to 55) MPa for benzene, tetrachloromethane, and the alkane series, from nonane to pentadecane. Experimental data were fitted to the next rational function of $T$ and $p$:

$$\alpha(p, T) = \frac{a_0 + a_1T + a_2T^2 + a_3T^3 + a_4p + a_5p^2}{1 + b_1T + b_2T^2 + b_3p} \tag{3}$$

For some liquids not all coefficients were needed; to determine the optimal number, an F-test was carried on. These coefficients as well as the standard deviations of the fits are presented in Table 1. Experimental values at representative temperatures and pressures are reported as Supporting Information.

With the aim of comparing the experimental results with available literature data, we obtained $\alpha_p$ from density correlations from refs 9 to 11 and 33 using the $\alpha_p$ definition:

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

The comparisons were carried out by making use of the average relative deviation, $\Delta$, defined as:

$$\Delta = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{Y_i^{\mathrm{exp}} - Y_i^{\mathrm{lit}}}{Y_i^{\mathrm{exp}}}\right| \tag{5}$$

where $Y$ stands for $\alpha_p$ and lit and exp denote literature and this work data, respectively. $\Delta$ was obtained only at the $T$ and $p$ of the Supporting Information. These deviations for all studied liquids are presented in Table 2. In addition, benzene data were compared with $\alpha_p$ results from Fuchs et al.,[18] directly obtained using a calorimetric method similar to that used in this work. A $\Delta$ value of 0.04 was obtained, which is significantly worse than that obtained from density data, for which the lowest $\Delta$ value among the liquids studied in this work was achieved. It is worth noting that density data for benzene is expected to be of very high quality, since it is obtained from a density fit of a lot of experimental data from assorted sources, and very good fits were obtained.[11] The worst coherence between literature and data of this work is for some of the heavier alkanes, for which the experimental database is relatively scarce, especially at high pressure.[10] These facts confirm the reliability of the reported experimental data.

**Table 1. Fitting Coefficients and Standard Deviations of the Fits *s* for the Studied Liquids**

| | Benzene | Tetrachloromethane | Nonane |
|---|---|---|---|
| $a_0/10^{-3}\ \mathrm{K^{-1}}$ | −0.1989 | 0.4238 | 0.6604 |
| $a_1/10^{-6}\ \mathrm{K^{-2}}$ | 9.5149 | 2.2705 | −1.3236 |
| $a_2/10^{-9}\ \mathrm{K^{-3}}$ | −36.7561 | −10.0778 | |
| $a_3/10^{-12}\ \mathrm{K^{-4}}$ | 37.9222 | 6.6332 | |
| $a_4/10^{-6}\ \mathrm{K^{-1} \cdot MPa^{-1}}$ | 1.3614 | 0.9392 | 0.4544 |
| $a_5/10^{-9}\ \mathrm{K^{-1} \cdot MPa^{-1}}$ | | | 1.1583 |
| $b_1/10^{-3}\ \mathrm{K^{-1}}$ | −2.3372 | −2.3116 | −3.3221 |
| $b_2/10^{-6}\ \mathrm{K^{-2}}$ | | | 2.6542 |
| $b_3/10^{-3}\ \mathrm{MPa^{-1}}$ | 3.0702 | 2.7238 | 2.1948 |
| $s/10^{-6}\ \mathrm{K^{-1}}$ | 2 | 3 | 2 |
| | Decane | Undecane | Dodecane |
| $a_0/10^{-3}\ \mathrm{K^{-1}}$ | 0.6595 | 0.6767 | 0.7001 |
| $a_1/10^{-6}\ \mathrm{K^{-2}}$ | −1.3345 | −1.3884 | −1.4375 |
| $a_2/10^{-9}\ \mathrm{K^{-3}}$ | | | |
| $a_3/10^{-12}\ \mathrm{K^{-4}}$ | | | |
| $a_4/10^{-6}\ \mathrm{K^{-1} \cdot MPa^{-1}}$ | 0.4031 | −0.2144 | 0.0774 |
| $a_5/10^{-9}\ \mathrm{K^{-1} \cdot MPa^{-1}}$ | 1.3581 | 3.1955 | 2.1909 |
| $b_1/10^{-3}\ \mathrm{K^{-1}}$ | −3.2560 | −3.1074 | −2.9457 |
| $b_2/10^{-6}\ \mathrm{K^{-2}}$ | 2.5102 | 2.1488 | 1.7860 |
| $b_3/10^{-3}\ \mathrm{MPa^{-1}}$ | 2.1055 | 1.4182 | 1.7750 |
| $s/10^{-6}\ \mathrm{K^{-1}}$ | 2 | 2 | 2 |
| | Tridecane | Tetradecane | Pentadecane |
| $a_0/10^{-3}\ \mathrm{K^{-1}}$ | 0.2154 | 0.5907 | 1.0855 |
| $a_1/10^{-6}\ \mathrm{K^{-2}}$ | 3.7490 | 1.3659 | −2.9730 |
| $a_2/10^{-9}\ \mathrm{K^{-3}}$ | −17.9027 | −11.5217 | 0.9858 |
| $a_3/10^{-12}\ \mathrm{K^{-4}}$ | 18.7676 | 13.6682 | 1.8196 |
| $a_4/10^{-6}\ \mathrm{K^{-1} \cdot MPa^{-1}}$ | 0.7983 | 1.2948 | 1.2902 |
| $a_5/10^{-9}\ \mathrm{K^{-1} \cdot MPa^{-1}}$ | | | |
| $b_1/10^{-3}\ \mathrm{K^{-1}}$ | −2.4785 | −2.1548 | −2.1396 |
| $b_2/10^{-6}\ \mathrm{K^{-2}}$ | | | |
| $b_3/10^{-3}\ \mathrm{MPa^{-1}}$ | 2.3186 | 3.7497 | 3.7319 |
| $s/10^{-6}\ \mathrm{K^{-1}}$ | 2 | 2 | 2 |

**Table 2. Δ for Isobaric Thermal Expansivities of All Studied Liquids**

| liquid | Δ |
|---|---|
| benzene | 0.006 |
| tetrachloromethane | 0.020 |
| nonane | 0.010 |
| decane | 0.009 |
| undecane | 0.051 |
| dodecane | 0.048 |
| tridecane | 0.011 |
| tetradecane | 0.017 |
| pentadecane | 0.023 |

Figure 1 shows selected $\alpha_p$ values as well as curve fits for all liquids as a function of pressure at several isotherms; $\alpha_p$ decreases against $p$ for all compounds. For some liquids there is a curve crossing at high pressure, which represents a change in temperature dependence, from positive at low pressures to negative at high pressures. This has been already obtained in previous papers devoted to the study of $\alpha_p$ against temperature and pressure.[15,17,18,20,23] Figure 2 shows $\alpha_p$ against $T$ for several isobars. The positive dependence against $T$ becomes less pronounced as pressure is raised, and for some liquids, (benzene,

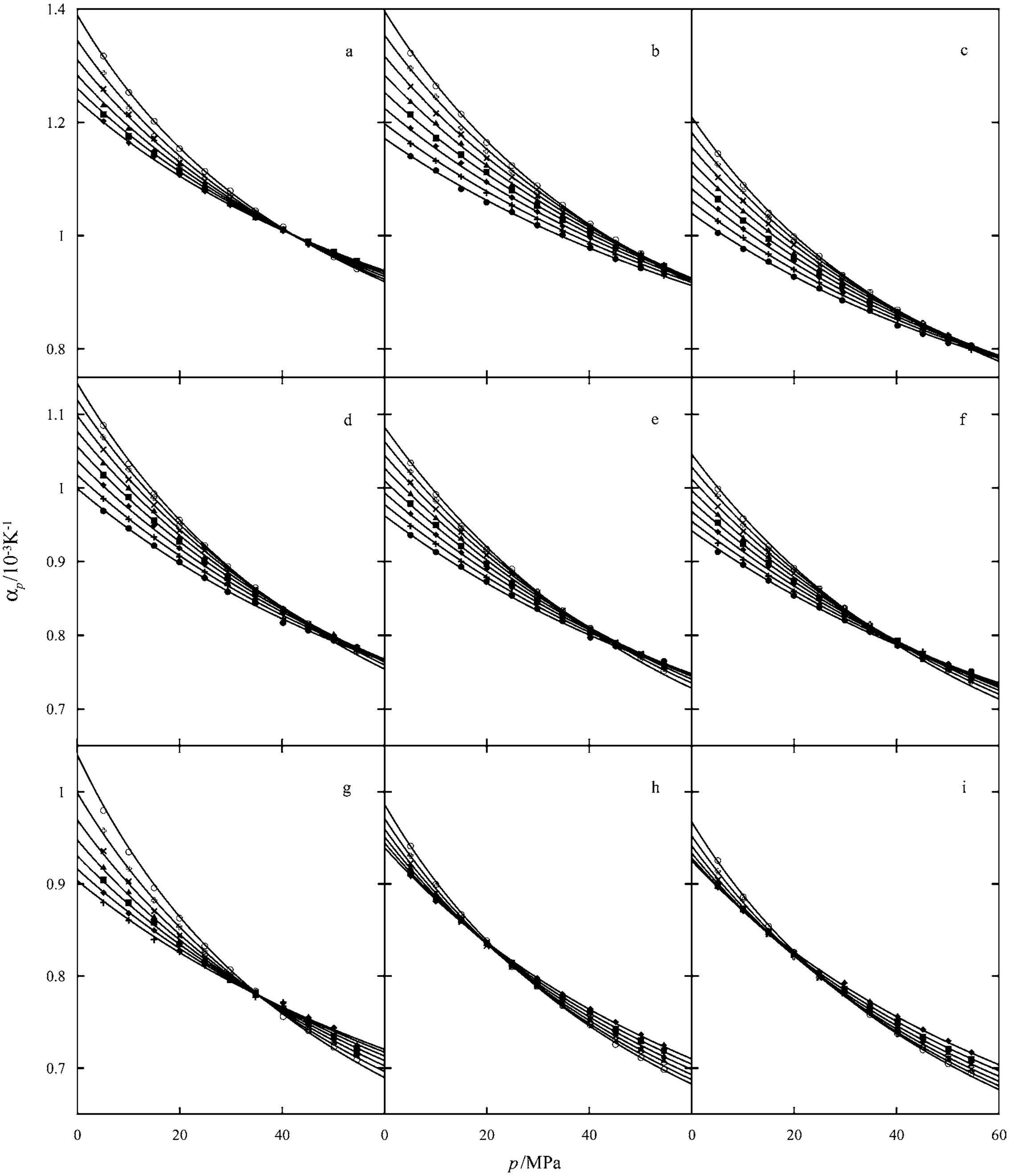

**Figure 1.** $\alpha_p$ values as a function of pressure at several temperatures for: (a) benzene; (b) tetrachloromethane; (c) nonane; (d) decane; (e) undecane; (f) dodecane; (g) tridecane; (h) tetradecane; (i) pentadecane. ●, $T$ = 278.15 K; +, $T$ = 288.15 K; ◆, $T$ = 298.15 K; ■, $T$ = 308.15 K; ▲, $T$ = 318.15 K; ×, $T$ = 328.15 K; open plus symbol, $T$ = 338.15 K; ○, $T$ = 348.15 K.

tridecane, tetradecane, and pentadecane) clear negative $T$ dependence at high pressure is obtained. Although milder, temperature also seems to have an effect on temperature dependency: at low pressure for some cases (again, benzene, tridecane, tetradecane, and pentadecane), positive $T$ dependence is more pronounced as temperature is higher, but as pressure is raised, this tendency disappears.

There is a close relation between isobaric thermal expansivity and fluctuations ($\alpha_p$ is proportional to enthalpy−volume cross-correlations), which become infinity at the critical point. Therefore, as the fluid is closer to its critical point, fluctuations become greater, and $\alpha_p$ increases. All fluids of this work are studied at temperatures well below $T_c$, and on the other hand, $p_c$ for all liquids is low, as compared with the experimental pressure range.[34,35] Therefore, for low pressure, increasing temperature implies approaching the critical point, which makes $\alpha_p$ increase, and as a consequence, $\alpha_p$ temperature dependence is positive. Nonetheless, as pressure is higher, the system begins to depart from critical conditions; fluctuations present lower importance, and $\alpha_p$ temperature dependence becomes milder. At a high enough pressure, the system becomes dominated by short-range repulsive forces, and fluctuations are negligible. Two examples of fluid models which, as a result of the absence of attractive forces, do not have a liquid−vapor phase transition are the ideal gas and the hard sphere fluid. In both cases, $\alpha_p$ decreases against $T$,[36] as a consequence of the lack of fluctuations. Therefore, fluids with lower vapor pressure and higher critical temperature must be, as a general rule, in a state less

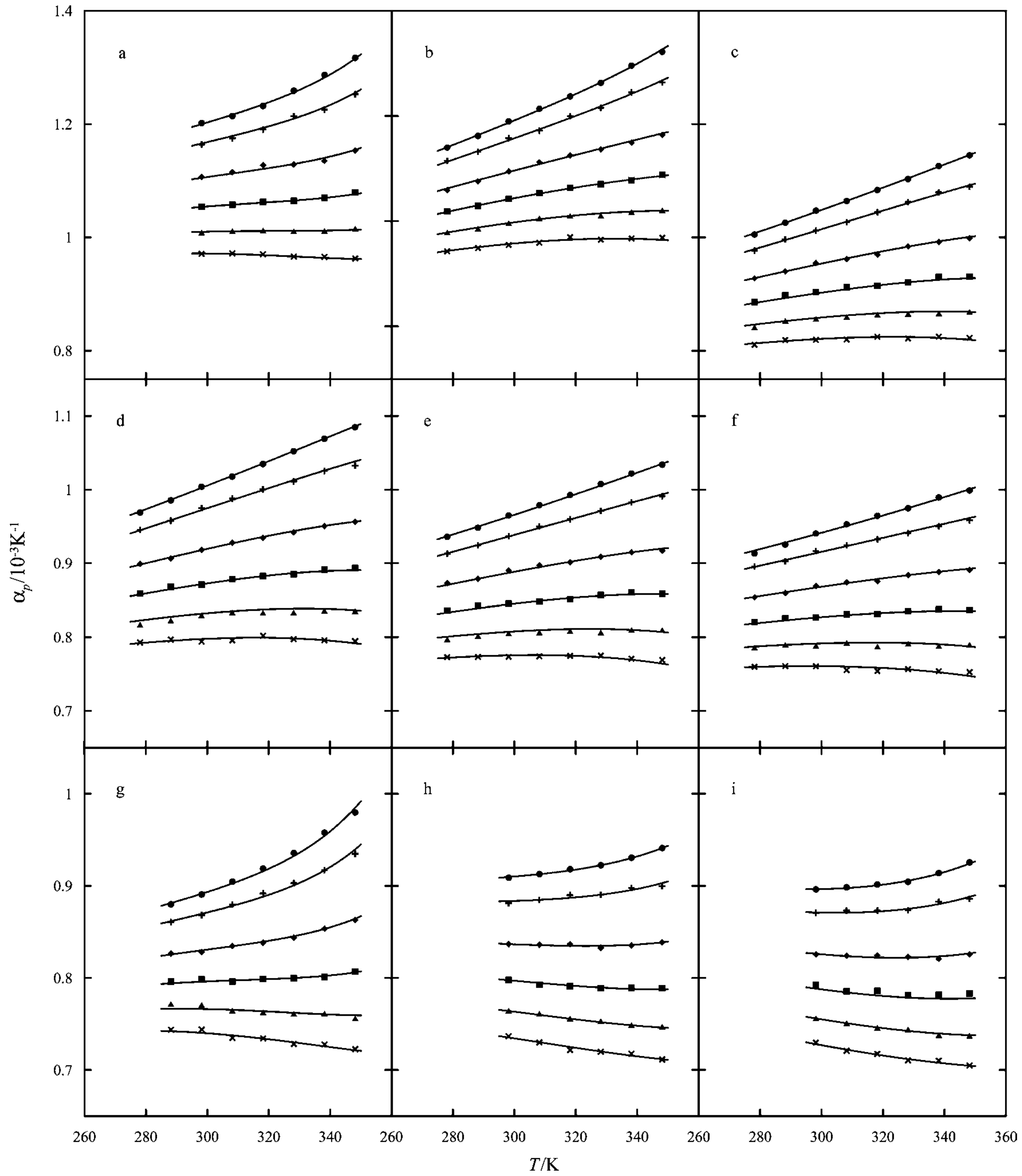

**Figure 2.** $\alpha_p$ values as a function of temperature at several pressures for: (a) benzene; (b) tetrachloromethane; (c) nonane; (d) decane; (e) undecane; (f) dodecane; (g) tridecane; (h) tetradecane; (i) pentadecane. ●, $p = 1$ MPa; +, $p = 10$ MPa; ◆, $p = 20$ MPa; ■, $p = 30$ MPa; ▲, $p = 40$ MPa; ×, $p = 50$ MPa.

affected by fluctuations than fluids with higher vapor pressure and lower critical temperature. As a consequence, for liquids with high $T_c$ and small $p_v$, a lower increase in pressure can easier induce negative $\alpha_p$ temperature dependence. This is what is observed for most of cases studied in this work: tetrachloromethane, the liquid with the highest vapor pressure ($p_v$ = 15.35 kPa[34]) and the lowest critical temperature ($T_c$ = 556.6 K[34]) does not show any change in its $\alpha_p$ temperature dependency; it remains positive over the whole temperature and pressure range, and the curve crossing seems to appear at pressures considerably higher than those of this work. For alkanes, the negative temperature dependency appears at lower pressure as alkyl chain is longer, which corresponds to an increment in critical temperature (it ranges from 594.56 K for nonane to 708.0 K for pentadecane[9,34]) and a decrement in vapor pressure (from 0.57 kPa for nonane to $3.5 \cdot 10^{-4}$ kPa for pentadecane[9,34,35]); in fact, there is no experimental evidence of such behavior for nonane and decane, although, with a view on the tendencies of the data, it is expected to be clearly observed at pressures not much higher than those of this work. The only exception to these trends is benzene: although it presents high $p_v$ (12.7 kPa[34]) and low $T_c$ (562.16 K[34]) values, a clear change in $\alpha_p$ temperature dependency is observed. Undoubtedly, $\alpha_p$ decreases against $T$ at a pressure as low as 40 MPa. It must be taken into account that the above-exposed general explanation of $\alpha_p$ results applies only for simple liquids, but it has been shown that those which present specific interactions could present a more complex $\alpha_p$ behavior.[17–24] Therefore, the observed departure from the general rule observed for benzene could be attributed to complex effects which could be ascribed to the aromatic nature of this compound; in fact,

**Table 3. Δ for Density of All Studied Liquids**

| liquid | Δ |
|---|---|
| benzene | 0.0002 |
| tetrachloromethane | 0.0005 |
| nonane | 0.0001 |
| decane | 0.0001 |
| undecane | 0.0010 |
| dodecane | 0.0007 |
| tridecane | 0.0004 |
| tetradecane | 0.0005 |
| pentadecane | 0.0002 |

unusual $\alpha_p$ behavior has been also observed for toluene, especially at low temperatures.[24]

***Derived Properties.*** Density, $\rho$, and isobaric heat capacity, $C_p$, can be calculated by making use of $\alpha_p$ data of this work. The density $\rho(T,p)$ can be obtained from integration of $\alpha_p$ using the next expression:

$$\rho(T, p) = \rho(T_0, p)\exp\left(-\int_{T_0}^{T}\alpha_p(T, p)\mathrm{d}T\right) \qquad (6)$$

where $\rho(T_0,p)$ is the density at a reference temperature $T_0$ and at pressure $p$. The integral $\int_{T_0}^{T}\alpha_p(T,p)\mathrm{d}T$ was calculated from $\alpha_p$ fits obtained from the data of the present work through eq 3. $T_0$ was selected to be 298.15 K, except for tridecane and pentadecane, because literature data[10] are available in temperature intervals of (303.15 to 473.15) K and (310.95 to 408.15) K; for these liquids, selected $T_0$ was (308.15 and 318.15) K, respectively. Once $\rho(T,p)$ was obtained from $\alpha_p$, it was compared with literature data.[10,11,33] Table 3 shows the average absolute deviation Δ of all studied liquids. Figure 3 shows the differences between experimental data and literature values against temperature for several isobars. Good coherence was obtained for most cases. The worst results are obtained for liquids which present high uncertainty in density[10,33] and at high temperature; this last effect probably arises from the uncertainty of $\alpha_p$, since

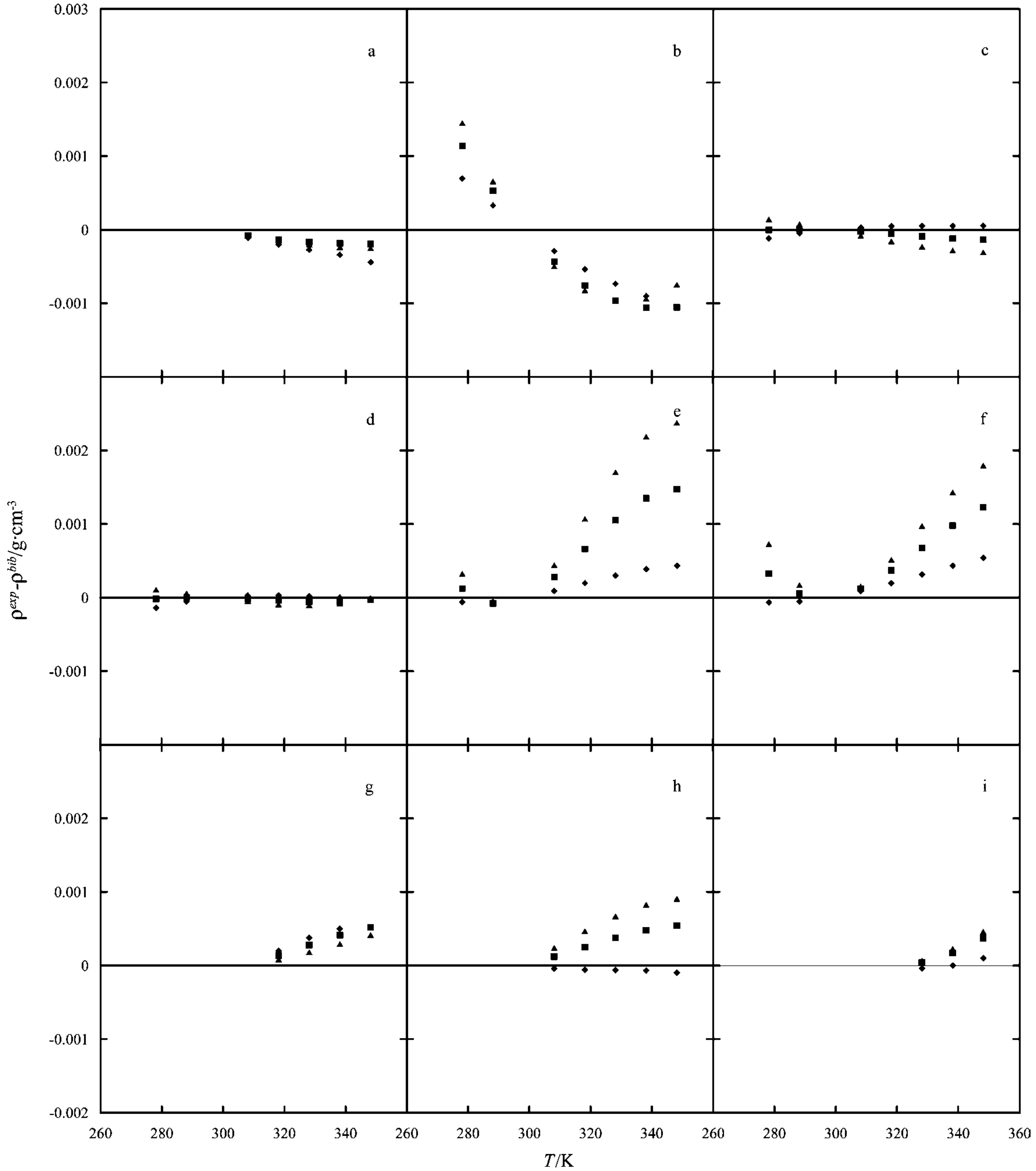

**Figure 3.** $\rho^{\mathrm{exp}} - \rho^{\mathrm{bib}}$ values as a function of temperature at several pressures for: (a) benzene; (b) tetrachloromethane; (c) nonane; (d) decane; (e) undecane; (f) dodecane; (g) tridecane; (h) tetradecane; (i) pentadecane. ◆, $p = 5$ MPa; ■, $p = 25$ MPa; ▲, $p = 50$ MPa.

**Table 4. Δ for Isobaric Molar Heat Capacity of All Studied Liquids**

| liquid | Δ[a] | Δ[b] |
|---|---|---|
| nonane | 0.0025 | |
| decane | 0.0024 | |
| undecane | 0.0010 | |
| dodecane | 0.0032 | 0.0019 |
| tridecane | 0.0024 | 0.0063 |
| tetradecane | 0.0006 | |
| pentadecane | | 0.0011 |

[a] Ref 31. [b] Refs 37 to 39.

it worsens to a great extent the accuracy of integrations as the temperature interval becomes wider.

Finally, from $\alpha_p$, $\rho$, molar mass $M$ and heat capacity at atmospheric pressure against temperature, $C_p(T,p_{\text{atm}})$, it is possible to obtain heat capacity as a function of temperature and pressure $C_p(T,p)$, on the basis of the next relation:

$$\left(\frac{\partial C_p(T,p)}{\partial p}\right)_T = -T\frac{M}{\rho(T,p)}\left(\alpha_p^2(T,p) + \left(\frac{\partial \alpha_p(T,p)}{\partial T}\right)_p\right) \tag{9}$$

$C_p(p,T)$ can be thus calculated from the next integral:

$$C_p(T,p) = C_p(T,p_{\text{atm}}) + \int_{p_{\text{at}}}^{p}\left(\frac{\partial C_p(T,p)}{\partial p}\right)\mathrm{d}p \tag{10}$$

$C_p(T,p)$ was obtained for those liquids for which directly measured $C_p$ at different pressures are available, which are nonane, decane, undecane, dodecane, tridecane, tetradecane, and pentadecane.[31,37–39] In eq 10 $C_p(T,p_{\text{atm}})$ was obtained from refs 31 and 37 to 39; $\rho(T,p)$ was calculated through Cibulka's correlations,[9,10] and $\alpha_p(T,p)$ was obtained from the fits of this work (eq 3). Table 4 shows the average deviations obtained from these calculations and data from literature. Figure 4 shows these comparisons for some studied liquids as a function of pressure at several temperatures. With a view on the stated uncertainty of directly measured $C_p(T,p)$ data, which are 0.2 % for Valencia's[31] and 0.5 % for Bessieres' data,[37–39] very good results were obtained for all studied liquids.

## Conclusion

The obtained $\alpha_p$ data have been revealed as highly precise, as a comparison with accurate literature data has shown. The results for nonpolar fluids reflect the $\alpha_p$ physical meaning (it is proportional to enthalpy−volume cross-correlations), as the comparison with phase transition properties has shown. The methodology is useful not only to accurately obtain $\alpha_p$ but also

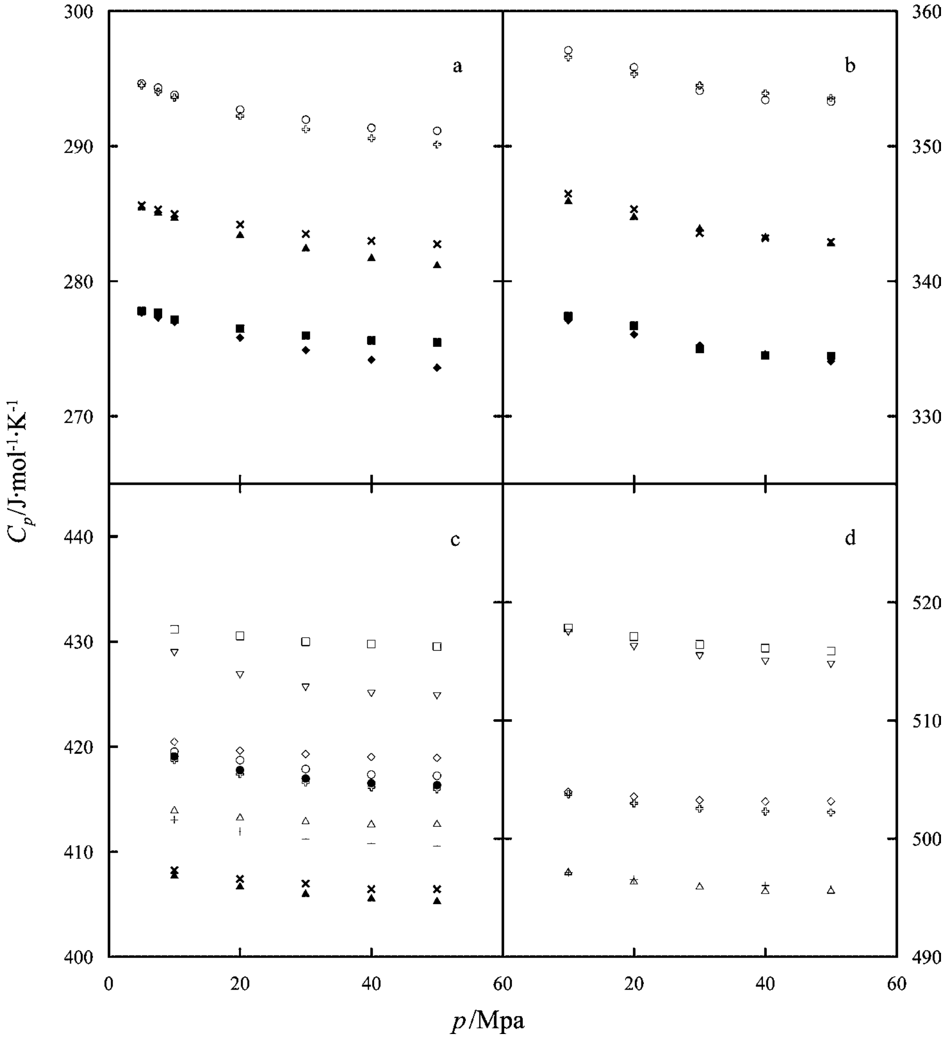

**Figure 4.** $C_p$ values as a function of pressure at several temperatures for: (a) nonane; (b) undecane; (c) tridecane; (d) pentadecane. This work data: ◆, $T$ = 283.15 K; ▲, $T$ = 303.15 K; +, $T$ = 313.15 K; open plus symbol, $T$ = 323.15 K using $C_p(T,p_{\text{atm}})$ from ref 25; ●, $T$ = 323.15 K using $C_p(T,p_{\text{atm}})$ from refs 38 and 39; ▽, $T$ = 343.15 K. Literature data: ■,[31] $T$ = 283.15 K; ×,[31] $T$ = 303.15 K; △,[31] $T$ = 313.15 K; ○,[31] ◇,[38,39] $T$ = 323.15 K; □,[38,39] $T$ = 343.15 K.

to determine density as a function of pressure and temperature, if this quantity is known as a function of pressure at some temperature, and also to calculate the isobaric molar heat capacity as a function of pressure and temperature, if this quantity is known as a function of temperature at some pressure (usually atmospheric) and density is known as a function of pressure and temperature.

**Note Added after ASAP Publication:** In the original version of the article published on the Web on November 17, 2009, some of the numerical values in Table 1 were incorrect. The corrected version was reposted on March 1, 2010.

**Supporting Information Available:**

Experimental data for thermal expansivities for the studied liquids as a function of temperature and pressure. This material is available free of charge via the Internet at http://pubs.acs.org.

## Literature Cited

(1) Sandarusi, J. A.; Mulia, K.; Yesavage, V. F. An automated flow calorimeter for the determination of liquid and vapor isobaric heat capacities: test results for water and n-pentane. *Rev. Sci. Instrum.* **1992**, *63*, 1810–1821.
(2) Rogers, P. S. Z.; Pitzer, K. S. High-temperature thermodynamic properties of aqueous sodium sulfate solutions. *J. Phys. Chem.* **1981**, *85*, 2886–2895.
(3) Bessieres, D.; Saint-Guirons, H.; Daridon, J.-L.; Coxam, J.-Y. Apparatus for simultaneous determination of the densities and heat capacities of liquids and of liquids with dissolved gas under an extended range of pressure (0.1−100 MPa). *Meas. Sci Technol.* **2000**, *11*, N69–N72.
(4) Abdulagatov, I. M.; Dvoryanchikov, V. I.; Kamalov, A. N. Measurements of the heat capacities at constant volume of $H_2O$ and($H_2O$ + $KNO_3$). *J. Chem. Thermodyn.* **1997**, *29*, 1387–1407.
(5) Khasanshin, T. S.; Shchamialiou, A. P.; Poddubskij, O. G. Thermodynamic Properties of Heavy n-Alkanes in the Liquid State: n-Dodecane. *Int. J. Thermophys.* **2003**, *24*, 1277–1289.
(6) Daridon, J. L.; Lagrabette, A.; Lagourette, B. Thermophysical properties of heavy synthetic cuts from ultrasonic speed measurements under pressure. *J. Chem. Thermodyn.* **1998**, *30*, 607–623.
(7) Daridon, J. L.; Lagourette, B.; Grolier, J.-P. E. Experimental measurements of the speed of sound in n-hexane from 293 to 373 K and up to 150 MPa. *Int. J. Thermophys.* **1998**, *19*, 145–160.
(8) Bessieres, D.; Saint-Guirons, H.; Daridon, J.-L. Thermophysical properties of n-tridecane from 313.15 to 373.15 K and up to 100 MPa from heat capacity and density data. *J. Therm. Anal. Calorim.* **2000**, *62*, 621–632.
(9) Cibulka, I. Saturated liquid densities of 1-alkanols from $C_1$ to $C_{10}$ and n-alkanes from $C_5$ to $C_{16}$: a critical evaluation of experimental data. *Fluid Phase Equilib.* **1993**, *89*, 1–18.
(10) Cibulka, I.; Hnedkovsky, L. Liquid densities at elevated pressure of n-alkanes from $C_5$ to $C_{16}$: A critical evaluation of experimental data. *J. Chem. Eng. Data* **1996**, *41*, 657–668.
(11) Cibulka, I.; Takagi, T. P-$\rho$-T Data of Liquids: Summarization and Evaluation. 5. Aromatic Hydrocarbons. *J. Chem. Eng. Data* **1999**, *44*, 411–429.
(12) Cibulka, I.; Zikova, M. Liquid Densities at Elevated Pressures of 1-Alkanols from C1 to C10: A Critical Evaluation of Experimental Data. *J. Chem. Eng. Data* **1994**, *39*, 876.
(13) Cerdeiriña, C. A.; Tovar, C. A.; González-Salgado, D.; Carballo, E.; Romaní, L. Isobaric thermal expansivity and thermophysical characterization of liquids and liquid mixtures. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5230–5236.
(14) Baonza, V. G.; Caceres Alonso, M.; Nuñez Delgado, J. Experimental and theoretical studies of the equation of state of liquid 2-butyne from 248 to 293 and pressure up to 104 MPa. *J. Phys. Chem.* **1992**, *96*, 1932–1938.
(15) Randzio, S. L.; Grolier, J. P. E.; Quint, J. R.; Eatough, D. J.; Lewis, E. A.; Hansen, L. D. n-Hexane as a model for compressed simple liquids. *Int. J. Thermophys.* **1994**, *15*, 415–41.
(16) Navia, P.; Troncoso, J.; Romaní, L. New calibration methodology for calorimetric determination of isobaric thermal expansivity of liquids as a function of temperature and pressure. *J. Chem. Thermodyn.* **2008**, *40*, 1607–1611.
(17) Ter Minassian, L.; Pruzan, P.; Soulard, A. Thermodynamic properties of water under pressure up to 5 kbar and between 28 to 120°C. Estimations in the supercooled region down to−40°C. *J. Chem. Phys.* **1981**, *75*, 3064–3072.
(18) Fuchs, A. H.; Pruzan, P.; Ter Minassian, L. Thermal expansion of benzene at high pressure determined by a calorimetric method, its behaviour near melting. *J. Phys. Chem. Solids* **1979**, *40*, 369–374.
(19) Randzio, S. L.; Grolier, J.-P. E.; Quint, J. R. Thermophysical properties of 1-Hexanol over the temperature range from 303 to 503 K and at pressures from the saturation line to 400 MPa. *Fluid Phase Equilib.* **1995**, *110*, 341–359.
(20) Alba, C.; Ter Minassian, L.; Denis, A.; Soulard, A. Reduction into a rational fraction of a thermodynamic property of the liquid state: Experimental determination in the case of $CO_2$ and *n*-butane. Extension to the other properties. *J. Chem. Phys.* **1985**, *82*, 384–393.
(21) Randzio, S. L.; Ter Minassian, L. Thermal expansion of coal-derived liquids. *Thermochim. Acta* **1987**, *113*, 67–72.
(22) Randzio, S. L.; Grolier, J.-P. E.; Quint, J. R. Isobaric thermal expansivities of binary mixtures of n-Hexane with 1-hexanol at pressures from 0.1 to 350 MPa and at temperatures from 303 to 503 K. *Int. J. Thermophys.* **1997**, *18*, 733–759.
(23) Randzio, S. L.; Hansen, L. D.; Lewis, E. A.; Eatough, D. J. Isobaric thermal expansivities of mixtures of m-cresol and quinoline from 0.1 to 400 MPa at 303 to 503 K. *Int. J. Thermophys.* **1997**, *18*, 1183–1195.
(24) Ter Minassian, L.; Bouzar, K.; Alba, C. Thermodynamic properties of liquid toluene. *J. Phys. Chem.* **1988**, *92*, 487–493.
(25) Randzio, S. L. From calorimetry to equations state. *Chem. Soc. Rev.* **1995**, *24*, 359–366.
(26) Navia, P.; Troncoso, J.; Romaní, L. Isobaric thermal expansivity of the binary system 1-hexanol + n-hexane as a function of temperature and pressure. *Fluid Phase Equilib.* **2009**, *276*, 1–6.
(27) Navia, P.; Troncoso, J.; Romaní, L. Isobaric thermal expansivity behaviour against temperature and pressure of associating fluids. *J. Chem. Thermodyn.* **2010**, *42*, 23–27.
(28) Navia, P.; Troncoso, J.; Romaní, L. Isobaric thermal expansivity for Ionic Liquids with a common cation as function of temperature and pressure. *J. Chem. Eng. Data* **2009**. DOI: 10.1021/je900407u.
(29) Navia, P.; Troncoso, J.; Romaní, L. Dependence against temperature and pressure of the isobaric thermal expansivity of Room Temperature Ionic Liquids. *J. Chem. Eng. Data*. DOI: 10.021/je900482x.
(30) Navia, P.; Troncoso, J.; Romaní, L. Isobaric thermal expansivity of highly polar nitrogen compounds. *J. Chem. Eng. Data*, submitted.
(31) Gonzalez-Salgado, D.; Valencia, J. L.; Troncoso, J.; Carballo, E.; Peleteiro, J.; Romani, L.; Bessieres, D. Highly precise experimental device for determining the heat capacity of liquids under pressure. *Rev. Sci. Instrum.* **2007**, *78*, 055103/1–055103/10.
(32) Wagner, W.; Pruss, A. The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use. *J. Phys. Chem. Ref. Data* **2002**, *31*, 387–531.
(33) Cibulka, I.; Takagi, T.; Ruzicka, K. P-$\rho$-T Data of Liquids: Summarization and Evaluation. 7. Selected Halogenated Hydrocarbons. *J. Chem. Eng. Data* **2001**, *46*, 2–28.
(34) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents: Physical properties and methods of purification*, Vol. II; Wiley: New York, 1986.
(35) Camin, D. L.; Rossini, F. D. Physical properties of 14 American petroleum institute research hydrocarbons $C_9$ to $C_{15}$. *J. Phys. Chem.* **1955**, *59*, 1173.
(36) Carnahan, N. F.; Starling, K. E. Equation of State for Nonattracting Rigid Spheres. *J. Chem. Phys.* **1969**, *51*, 635–636.
(37) Bessières, D.; Saint-Guirons, H.; Daridon, J.-L. High pressure measurement of n-dodecane heat capacity up to 100 MPa. Calculation from equations state. *High Pressure Res.* **2000**, *18*, 279–284.
(38) Bessières, D.; Saint-Guirons, H.; Daridon, J.-L. Thermophysical properties of n-tridecane from 313.15 to 373.15 and up to 100 MPa from heat capacity and density data. *J. Therm. Anal. Calorim.* **2000**, *62*, 621–632.
(39) Bessières, D.; Saint-Guirons, H.; Daridon, J.-L. Thermophysical properties of liquid n- pentadecane. *Phys. Chem. Liq.* **2001**, *39*, 301–313.

Received for review September 18, 2009. Accepted October 28, 2009. The authors are grateful to the Dirección Xeral de I + D da Xunta de Galicia (Projects PGIDIT-06-PXIB-3832828-PR and INCITE08E1R383012ES) and Universidad de Vigo (Project 08 VI-A12) for financial support. Assistance to P.N. by Xunta de Galicia (Project PGIDIT-06-PXIB-3832828-PR) is greatly appreciated. Authors want to thank Clara M. Fernández-Rodríguez for technical assistance.

JE900757K