Determination of Isobaric Thermal Expansivity of Organic Compounds from 0.1 to 30 MPa at 30 °C with an Isothermal Pressure Scanning Microcalorimeter

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This paper describes a simple high-pressure mercury-free microcalorimetric technique that enables the compression of a fluid from 0.1 to 30 MPa. Thermal expansivities of several compounds were calculated (*n*-hexane, cyclohexane, heptane, and toluene) with the pressure scanning transitiometry method at 30 °C ± 0.03 °C as a function of pressure and compared to the data found in the literature. The results are quite close to the literature values (4.2% at the very worst), and the uncertainty has been evaluated at 2%. A Tait equation, fitted from experimental density data, was also used to test the results of this work. The difference is between −5.9% and 3.2%.

Introduction

Isobaric thermal expansivity is an important thermodynamic parameter. It can help in calculating various thermodynamic properties and can be used in different models such as the Flory theory of liquids.

Thermal expansivities of most compounds are available at 0.1 MPa, but such data seem to be scarce as a function of pressure. Several techniques are available to calculate such a parameter as a function of pressure. First, density can be measured at different pressures and temperatures, and the thermal expansivity is deduced from these measurements. For instance, Calado et al.[1] determined the thermal expansivity of liquid ethylene with that technique from 0.5 to 130 MPa using an equation of state. Thermal expansivity can also be calculated from speed-of-sound measurements. Davis and Gordon[2] initiated this technique in calculating the thermal expansivity of mercury. Another way is with microcalorimetry. Pruzan et al.[3,4] and Randzio[5] adjusted two slightly different techniques, as described below.

In the present paper, a new simple technique based on microcalorimetry using scanning transitiometry is applied to directly measure the enthalpy of compression for four hydrocarbon fluids. The results have been compared with thermal expansivities measured with three different techniques: a computational method from speed-of-sound data, the piezothermal analysis, and the scanning transitiometry.

Theory

For one mole of pure substance, the enthalpy differential can be described by the following equations:

$$dH(T,P) = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \tag{1}$$

$$dH(T,P) = \delta q + V_m \, dP \tag{2}$$

where H is the molar enthalpy, V_m the molar volume, P the pressure, T the temperature, and q the molar heat.

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When T is kept constant, $dT = 0$, so eqs 1 and 2 reduce to the following one:

$$\delta q = \left[\left(\frac{\partial H}{\partial P}\right)_T - V_m\right] dP \tag{3}$$

Furthermore, from the Maxwell thermodynamical equations, we have

$$\left(\frac{\partial H}{\partial P}\right)_T - V_m = \left(\frac{\partial S}{\partial P}\right)_T T = -\left(\frac{\partial V_m}{\partial T}\right)_P T \tag{4}$$

So, eq 3 can now be written as

$$\delta q = -\left(\frac{\partial V_m}{\partial T}\right)_P T \, dP \tag{5}$$

For n moles of pure substance, the heat δQ released during an isothermal compression of dP is

$$\delta Q = -n\left(\frac{\partial V_m}{\partial T}\right)_P T \, dP \tag{6}$$

If a liquid sample of n moles of pure substance is compressed in a vessel, for which the volume is V, the resulting heat quantity that is exchanged with a thermostat at temperature T is given by eq 7:

$$\delta Q = -n\left(\frac{\partial V_m}{\partial T}\right)_P T \, dP = -\frac{V}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_P T \, dP = -\alpha V T \, dP \tag{7}$$
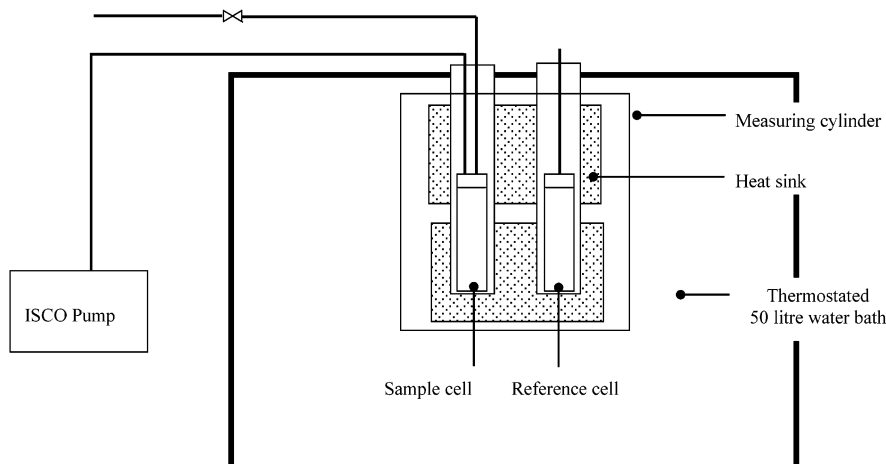
where V is the internal volume of the calorimetric vessel and $\alpha = (1/V_m)(\partial V_m/\partial T)_P$ is the isobaric thermal expansivity of the substance under investigation.

However, the heat released by the deformation of the vessel cannot be neglected[3] and can be estimated as follows:

$$dV_V = \left(\frac{\partial V_V}{\partial T}\right)_P dT + \left(\frac{\partial V_V}{\partial P}\right)_T dP$$

where V_V is the volume of the steel of the vessel.

Figure 1. Schematic representation of the high-pressure microcalorimeter.

However, T is constant, so we have

$$\mathrm{d}V = \left(\frac{\partial V}{\partial P}\right)_T \mathrm{d}P = -V\kappa_{T,V}\,\mathrm{d}P \qquad (8)$$

where $\kappa_{T,V}$ is the isothermal coefficient of compressibility of the material from which the vessel is made. From the Maxwell relation $(\partial S/\partial V)_T = (\partial P/\partial T)_V = \alpha_V/\kappa_{T,V}$, eq 9 is obtained, which defines the heat released by the walls of the vessel δQ_V:

$$\delta Q_V = T\,\mathrm{d}S_V = T\frac{\alpha_V}{\kappa_{T,V}}\,\mathrm{d}V_V = -\alpha_V VT\,\mathrm{d}P \qquad (9)$$

The heat released by the only compression of the fluid is finally

$$\delta Q = -\alpha VT\,\mathrm{d}P - \delta Q_V = -(\alpha - \alpha_V)VT\,\mathrm{d}P \qquad (10)$$

Several methods are available to determine experimentally the expansivity. Davis and Gordon[2] initiated the first method in 1967. Density, heat capacity, thermal expansivity, and isothermal compressibility are calculated from the measured values of the sound velocity. However, this method uses some integrals and requires some approximations (linearity of the thermal expansivity over a pressure interval for instance). The second one is called the piezo-thermal method and was developed by Pruzan et al.[3,4] in 1976. Pressure is applied inside the calorimeter in a few bar steps, and the resulting thermograms giving δQ and $(\alpha - \alpha_V)$ are calculated using eq 10. According to Randzio et al.,[6] this method may be inaccurate because of the manual changes of pressure.

Randzio[5] has developed another method, called scanning transitiometry. If P is a linear function of time, eq 10 may be written

$$\frac{\delta Q}{\mathrm{d}t}\Big|_T = -(\alpha - \alpha_V)VT\frac{\mathrm{d}P}{\mathrm{d}t} \qquad (11)$$

This method was chosen in the present work.

Experimental Section

An isothermal microcalorimeter LKB 2277 bioactivity monitor, equipped with specially designed high-pressure cells, was used. It is based on the "heat flow" principle. The measuring cylinders are suspended in a 50 L water bath, each cylinder containing metal heat sinks and a pair of measuring cells. The measuring cells operate in pairs, with one cell used as a reference and the other containing the sample.

The original sample cell was not designed to work under pressure. So a new one was designed (Sanchez Technologies, France) so as to be able to work at 30 MPa. It is made of stainless steel 316 S. The external dimensions of the cell are 60 mm × 13.9 mm, and its volume is equal to 2.96 cm^3 ± 0.02 cm^3. Two stainless steel tubes (inner diameter = 0.25 mm) are welded to the lid of the cell. They enable the filling of the cell and the ejection of gas bubbles. The reference cell is an exact copy of the sample cell. The measuring vessel is enclosed by metal heat sinks that are kept at a constant temperature. The range of temperature is 20 to 80 °C. Sandwiched between the measuring vessel and the heat sink is a pair of Peltier elements that are thermoelectric generators. They create a detectable voltage proportional to the difference of temperature between the measuring vessel and the heat sink. Figure 1 represents this apparatus.

According to eq 10, two parameters are important: the cell volume and the expansivity of the vessel itself.

To determine the contribution of the vessel itself to the overall heat effect, an Invar cylindrical rod occupying approximately 90% of the volume was inserted in the vessel, as proposed Pruzan et al.[3] Invar has a very low thermal expansivity (for Invar 36, $\alpha_V = 1.18 \times 10^{-6}$ K^{-1} in the temperature range 25–100 °C).

If the heat effect of the compression of the Invar rod is neglected, we have

$$\delta Q = -\alpha_{\mathrm{liq}}(V_{\mathrm{cell}} - V_{\mathrm{Invar}})T\,\mathrm{d}P + \alpha_V V_{\mathrm{cell}} T\,\mathrm{d}P \qquad (12)$$

So,

$$\delta Q = -V_{\mathrm{cell}} T\,\mathrm{d}P\left[\alpha_{\mathrm{liq}}\left(1 - \frac{V_{\mathrm{Invar}}}{V_{\mathrm{cell}}}\right) - \alpha_V\right] \qquad (13)$$

Distilled water was used to pressurize the cell. The thermal expansivity of water determined by Ter Minassian et al.[7] was used. The thermal expansivity of the cell α_V was found equal to that value:

$$\alpha_V = 1.87 \times 10^{-5}\ \mathrm{K}^{-1}$$

According to Bogaard et al.,[8] this value seems to be in the right range. Table 1 gives some values of the cubic expansivity of the stainless steel used in the literature. It is assumed not to depend on the pressure. This parameter
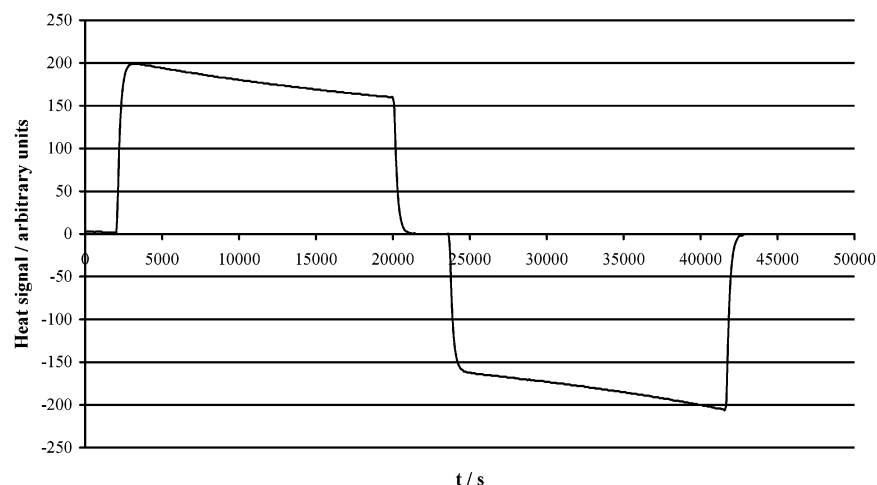
Figure 2. Example of a thermogram during the compression and the decompression of hexane at 30 °C between 0.1 and 30 MPa.

Table 1. Thermal Expansivities of Stainless Steel in the Literature

ref	stainless steel quality	$10^5\alpha$/K^{-1}
Pruzan et al.[3]	not indicated	1.60
this work	316	1.87
Ter Minassian et al.[4]	not indicated	4.80
Randzio et al.[6]	304	5.51
Randzio et al.[9]	304	5.10

Table 2. Uncertainty of the Different Sensors

signal	sensor	range	uncertainty
pressure	ISCO pump	0.7–514 bar	±0.5% of full scale
temperature	microcalorimeter	20–80 °C	0.03 °C
time	computer		0.01 s
heat signal	microcalorimeter	0.15–3000 μW	0.1%

is very important, and most of the differences with the literature data may come from its variations.

Calibration of the thermal heat trace of the calorimeter was made using the built in calibration unit, applying powers in the range from 3 to 3000 μW.

Then, to exert the pressure in the sample cell, the fluid itself is used and the pressure is established by means of a high-pressure syringe pump (ISCO pump 260 D). The cell is filled at a constant flow with the compound under investigation so as to expel any air. If the pressure–volume curve of the fluid during the compression is not a straight line, it indicates the presence of a gas phase in the cell. After thermal equilibrium is reached, the fluid is pressurized while recording the heat evolution. Table 2 presents the uncertainties of the different sensors. The fluid can be compressed at different rates (between 0.1 MPa/min and 0.25 MPa/min in this work). The heat effects in the capillary connections are assumed to be negligible (a slow compression decreases these effects), and the measured heat quantities are said to arise exclusively from the volume of sample contained in the internal volume of the cell (the volume of fluid in the connections represents 1% of the volume of the cell). Figure 2 represents a thermogram obtained during the compression and the decompression of *n*-hexane.

Chemicals

Several organic compounds were studied so as to evaluate the reliability of the high-pressure device. Table 3 summarizes the properties and the origin of the compounds under investigation.

Table 3. Origin of the Compounds

compound	supplier	purity/wt %
heptane	Rathburn chemicals	>99.7
cyclohexane	Rathburn chemicals	>99.8
toluene	Rathburn chemicals, dried with molecular sieves	>99.8
hexane	JT Baker	>99

Table 4. Thermal Expansivities of *n*-Hexane as a Function of Pressure at 30 °C

P	$10^3\alpha$	abs dev[a]	$10^3\alpha_{lit.}$[3,9][b]	diff[c]
bar	K^{-1}	%	K^{-1}	%
5	1.353	0.2	1.365[3]	0.9
10	1.347	0.2		
20	1.330	0.2		
27	1.319	0.2	1.289[3]	−2.3
40	1.299	0.1		
49	1.287	0.1	1.304[3]	1.3
60	1.262	1.0		
70	1.250	0.8		
80	1.237	0.8		
90	1.221	0.9		
100	1.210	0.8		
110	1.198	0.8		
120	1.187	0.8		
130	1.176	0.6		
141	1.164	0.6	1.216[9]	4.2
145	1.161	0.6	1.181[3]	1.7
160	1.147	0.5		
170	1.137	0.5		
180	1.127	0.4		
190	1.118	0.4		
200	1.110	0.4		
210	1.100	0.3		
220	1.092	0.2		
230	1.083	0.2		
245	1.071	0.2	1.094[3]	2.1
250	1.069	0.3		
260	1.060	0.3		
270	1.053	0.3		
280	1.045	0.3		
290	1.039	0.3		
300	1.033	0.4		

[a] Absolute deviation = (average of the absolute deviation of data points from their mean)/arithmetic mean. [b] In ref 3, T = 301.5 K, and in ref 9, T = 303.15 K. [c] Difference = (literature − results)/literature.

Results and Discussion

Each compound had been compressed at least six times at different rates of pressure variations. Tables 4–7 present the results. For each compound, the thermal expansivity

Table 5. Thermal Expansivities of Cyclohexane as a Function of Pressure at 30 °C

P	$10^3\alpha$	A.D.	$10^3\alpha_{lit.}$ [10] ^{a}	diff
bar	K^{-1}	%	K^{-1}	%
5	1.176	0.1		
10	1.172	0.2		
20	1.163	0.0		
30	1.152	0.1		
40	1.145	0.0		
50	1.135	0.2	1.176	3.5
60	1.126	0.3		
70	1.118	0.4		
80	1.109	0.2		
90	1.103	0.2		
100	1.092	0.5	1.132	3.6
110	1.087	0.3		
120	1.079	0.1		
130	1.072	0.2		
140	1.065	0.3		
150	1.058	0.2	1.092	3.2
160	1.052	0.2		
170	1.045	0.3		
180	1.038	0.2		
190	1.032	0.2		
200	1.025	0.2	1.056	2.9
210	1.018	0.2		
220	1.012	0.1		
230	1.007	0.2		
240	1.001	0.3		
250	0.994	0.4	1.024	2.8
260	0.988	0.4		
270	0.985	0.2		
280	0.977	0.3		
290	0.975	0.1		
300	0.970	0.0	0.993	2.3

^{a} In ref 10, T = 303.15 K.

Table 6. Thermal Expansivities of Heptane as a Function of Pressure at 30 °C

| P	$10^3\alpha$	A.D.	$10^3\alpha_{lit.}$ [11] ^{a}	diff
bar	K^{-1}	%	K^{-1}	%
5	1.250	0.0	1.280	2.3
10	1.243	0.00		
20	1.231	0.0		
30	1.218	0.1		
40	1.208	0.1		
50	1.188	0.8		
60	1.177	0.7		
70	1.167	0.6		
80	1.157	0.6		
90	1.147	0.6		
100	1.137	0.5		
110	1.127	0.4		
120	1.119	0.5		
130	1.109	0.4		
140	1.099	0.4		
150	1.092	0.3		
160	1.084	0.4		
170	1.075	0.3		
180	1.067	0.3		
190	1.060	0.3		
200	1.050	0.2	1.085	3.2
210	1.043	0.2		
220	1.036	0.3		
230	1.028	0.2		
240	1.021	0.2		
250	1.014	0.2		
260	1.006	0.3		
270	1.002	0.2		
280	0.995	0.2		
290	0.988	0.2		
300	0.983	0.2	1.023 ^{b}	3.9

^{a} In ref 11, extrapolation between T = 295 K and T = 310 K. ^{b} Extrapolation between 200 and 400 bar.

is presented as a function of pressure, as well as the absolute deviation of the different measurements [average of the absolute deviation of data points from their mean/arithmetic mean]. Then, the results are compared to literature data. The uncertainty of the results of this work

Table 7. Thermal Expansivities of Toluene as a Function of Pressure at 30 °C

P	$10^3\alpha$	A.D.	$10^3\alpha_{lit.}$ [12] ^{a}	diff [12]	$10^3\alpha_{lit.}$ [13] ^{b}	diff [13]
bar	K^{-1}	%	K^{-1}	%	K^{-1}	%
5	1.044	0.1	1.083 ^{c}	3.6	1.023	−2.4
10	1.039	0.1			1.020	−2.3
20	1.033	0.1			1.014	−2.3
30	1.026	0.1			1.008	−2.1
40	1.020	0.1			1.002	−1.8
50	1.012	0.2			0.996	−1.7
60	1.007	0.1			0.991	−1.7
70	1.002	0.1			0.986	−1.7
80	0.996	0.1			0.980	−1.6
90	0.990	0.2			0.975	−1.5
100	0.984	0.2			0.970	−1.5
110	0.977	0.2			0.965	−1.4
120	0.973	0.3			0.960	−1.5
130	0.967	0.2			0.955	−1.4
140	0.962	0.2			0.950	−1.4
150	0.957	0.3			0.945	−1.3
160	0.952	0.3			0.940	−1.3
170	0.947	0.3			0.936	−1.3
180	0.942	0.3			0.931	−1.2
190	0.937	0.3			0.927	−1.2
200	0.932	0.3	0.972	4.1	0.922	−1.1
210	0.928	0.3			0.918	−1.2
220	0.923	0.3			0.914	−1.1
230	0.918	0.3			0.909	−1.1
240	0.914	0.5			0.905	−1.1
250	0.908	0.6			0.901	−1.0
260	0.904	0.6			0.897	−0.9
270	0.903	0.3			0.893	−1.3
280	0.896	0.5			0.889	−1.0
290	0.896	0.3			0.885	−1.4
300	0.892	0.3			0.881	−1.4

^{a} In ref 12, T = 300 K. ^{b} In ref 13, T = 303.15 K. ^{c} This value is at P = 1 bar.
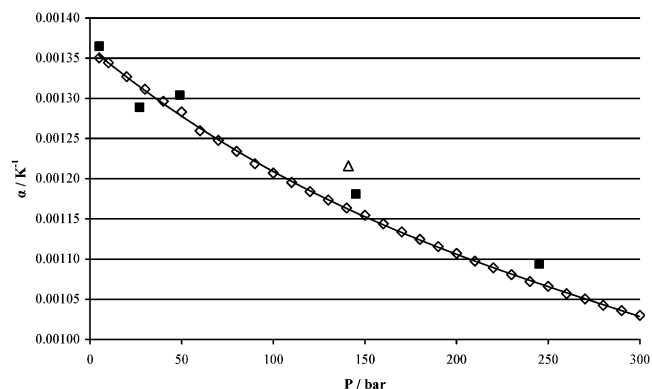
Figure 3. Thermal expansivities of hexane as a function of pressure at 30 °C: ◇, this work; ■, Pruzan et al.;[3] △, Randzio et al.[9]

has been estimated at 2%, and it is mainly due to the perturbations of the heat signal (noise).
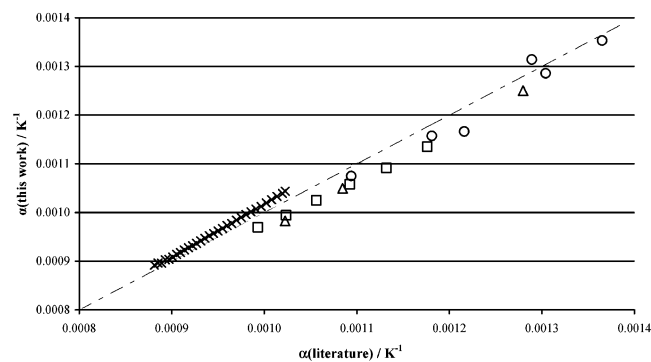
n-Hexane data were compared with the ones calculated by Randzio et al.[9] (T = 303.15 K) with the pressure scanning method and by Pruzan et al.[3] (T = 301.5 K) with the piezothermal analysis. The accuracy in ref 3 is said to be about 2%. The difference with the literature data reaches 2.3% with ref 3 and 4.2% with ref 9. Figure 3 represents the thermal expansivity calculated in this work, the literature data as well as those from a simple third order polynomial model. Table 8 gives the coefficients of this polynomial equation for each investigated compound and the average of the absolute deviation (AAD) between the results and the model.

Cyclohexane data were compared to the ones presented by Sun et al.[10] (T = 303.15 K). These data were calculated with Davis and Gordon's method. The difference varies between 2.3 and 3.6%.

Table 8. Third Order Polynomial Equation of the Thermal Expansivity of Several Compounds at 30 °C between 5 and 300 bar

$\alpha(T = 303.15 \text{ K})/\text{K}^{-1} = a(P/\text{bar})^3 + b(P/\text{bar})^2 + c(P/\text{bar}) + d$				
	$10^{12}a$	$10^9 b$	c	$10^3 d$	AAD[a]
compound	$\text{K}^{-1}\cdot\text{bar}^{-3}$	$\text{K}^{-1}\cdot\text{bar}^{-2}$	$\text{K}^{-1}\cdot\text{bar}^{-1}$	K^{-1}	%
n-hexane	−4.281	3.832	-1.878×10^{-6}	1.3654	0.10
cyclohexane	−0.7634	1.112	-9.733×10^{-7}	1.1811	0.06
n-heptane	−2.985	2.615	-1.437×10^{-6}	1.2575	0.10
toluene	0.2900	0.3920	-6.598×10^{-7}	1.0458	0.07

[a] AAD = average of the absolute deviation.

Figure 4. Comparison between literature and experimental data: △, *n*-heptane; □, cyclohexane; ○, *n*-hexane; ×, toluene.

n-Heptane data were compared to the ones presented by Murringer et al.[11] (extrapolation between $T = 295$ K and $T = 310$ K). These data were calculated with Davis and Gordon's method. The difference varies between 2.3 and 3.9%.

Toluene data were compared with the ones calculated by Sun et al.[12] ($T = 300$ K) with Davis and Gordon's method and by Ter Minassian et al.[13] ($T = 303.15$ K) with piezothermal analysis. The difference with the first method is between 3.6 and 4.1%, and that for the second one is between −2.4% and −1%.

Figure 4 compares the results to the literature data. One can see that the results are below the literature values for most compounds except for toluene. This can be explained by the accuracies of the different methods used, the uncertainty of the calibration of the microcalorimeter, and slight differences in the conditions of the literature measurements (temperature and pressure), but it is mainly explained by the values of the expansivity of the stainless steel.

It can be interesting to evaluate the influence of the expansivity of the stainless steel with more accuracy. The following parameter was calculated for each compound under investigation at different values of thermal expansivity of stainless steel:

$$a = \text{average}\left(\left|\frac{\alpha(\text{lit.}) - \alpha(\text{this work})}{\alpha(\text{lit.})}\right|\right)$$

Figure 5 represents that parameter as a function of thermal expansivity of stainless steel for the studied compounds. There is no general behavior: the average difference of *n*-heptane decreases with α_V whereas the one of toluene increases. The total average has been made for all the compounds and reaches a minimum for $\alpha_V = 4.80 \times 10^{-5}$ K^{-1}. However, with more compounds, another minimum may be found. So, it seems inappropriate to choose that minimum rather than the value determined by the Invar rod method.
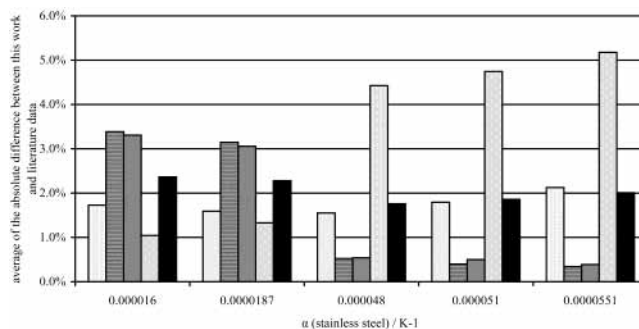
Figure 5. Influence of the thermal expansivity of stainless steel. From left to right for each group of bars: *n*-hexane, *n*-heptane, cyclohexane, toluene, total average.
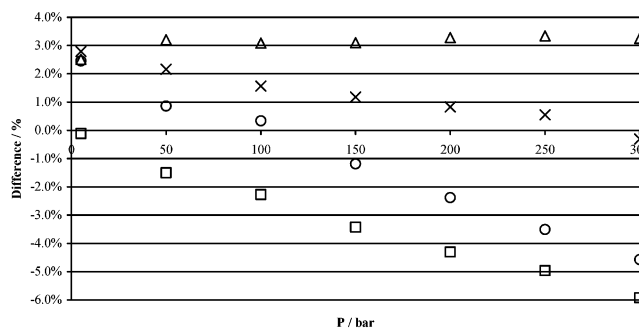
Figure 6. Difference between thermal expansivities of this work and thermal expansivities obtained from the Tait equation: △, *n*-heptane; □, cyclohexane; ○, *n*-hexane; ×, toluene. The difference is calculated as follows: (Tait equation − this work)/Tait equation.

It also appeared relevant to use an equation of state so as to study the reliability of the results of this work. Actually, experimental data of thermal expansivities as a function of pressure are quite scarce, so an equation of state is a good alternative. Cibulka et al.[14,15] reviewed experimental density data as a function of pressure and fitted them by a Tait equation:

$$\rho(P,T) = \frac{\rho_0(T)}{1 - C(T) \ln\left(\dfrac{B(T) + P}{B(T) + P_0}\right)} \quad (14)$$

where $\rho_0(T)$ is the density at $P = 0.1$ MPa, C and B are functions of temperature, P is the pressure, and $P_0 = 0.1$ MPa.

Thus, thermal expansivity can be calculated from density:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P \quad (15)$$

The density at $P = 1$ bar is calculated from DIPPR correlations. $B(T)$ and $C(T)$ are calculated from equations given by Cibulka et al.[14,15]

Figure 6 shows the difference between the thermal expansivities measured in this work and the ones calculated from the Tait equation as a function of pressure. For *n*-hexane, the difference is between 2.5% at 0.5 MPa and −4.6% at 30 MPa. For cyclohexane, the difference is between −0.1% at 0.5 MPa and −5.9% at 30 MPa. For *n*-heptane, the difference is between 2.5% at 0.5 MPa and 3.2% at 30 MPa. For toluene, the difference is between 2.8% at 0.5 MPa and −0.3% at 30 MPa.

There is no systematic deviation between the results of this work and the results obtained from the Tait equation.

For instance, the Tait equation overestimates the thermal expansivity of *n*-heptane but underestimates the one of cyclohexane. Furthermore, so as to check the accuracy of the Tait equation, Cibulka et al.[15] calculated isothermal compressibilities at $P = 0.1$ MPa and at different temperatures. For toluene, the difference is between -1% and -3.4% at $T = 303.15$ K according to the different experimental data. So, the Tait equation of state provides more data, but those data are not more relevant than experimental ones because that equation implies uncertainties as well.

As a conclusion, one can say that the developed high-pressure mercury-free microcalorimetric technique gives relevant results, considering the comparison with the literature. The assumption according to which heat effects in the tubes are negligible seems to be correct.

Acknowledgment

Symbols

B = Tait equation parameter, Pa
C = Tait equation parameter, unitless
H = molar enthalpy, J·mol^{-1}
n = number of moles, mol
P = pressure, Pa
P_0 = standard pressure, Pa
q = molar heat, J·mol^{-1}
Q = heat, J
S = molar entropy, J·K^{-1}·mol^{-1}
t = time, s
T = temperature, K
V = volume, m^3
V_m = molar volume, m^3·mol^{-1}
V_V = volume of the vessel, m^3
α = isothermal expansivity, K^{-1}
α_v = isothermal expansivity of the cell, K^{-1}
κ_T = isothermal compressibility, Pa^{-1}
$\kappa_{T,V}$ = isothermal compressibility of the vessel, Pa^{-1}
ρ = density, kg·m^{-3}
ρ_0 = density at the standard pressure, kg·m^{-3}

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