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THE STUDY OF STEREOISOMERISM INFLUENCE ON SPEED OF SOUND, ISENTROPIC COMPRESSIBILITY AND HEAT CAPACITY

Application to *cis*-decalin and *trans*-decalin

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In order to study the influence of stereoisomerism on thermodynamic derived properties, an extensive experimental study has been carried out for the two stereoisomers of decahydronaphthalene known as *cis*- and *trans*-decalin. For both compounds, speed of sound data are reported up to 150 MPa in the temperature range 303.15 to 373.15 K. Heat capacity measurements are presented up to 60 MPa for temperature ranging from 313.15 to 383.15 K. The experimental speed of sound together with the heat capacity data were used to estimate densities and compressibilities of the fluids up to 150 MPa. The thermodynamic consistency between volumetric, acoustical and calorimetric properties is then checked. The effect of stereoisomerism on speed of sound, isentropic compressibility and heat capacity behaviours is analyzed. It is concluded that the influence observed on these thermodynamic properties mainly results from volumetric effects.

Keywords: *decalin, heat capacity, isentropic compressibility, speed of sound, stereoisomerism*

Introduction

Stereoisomerism refers to compounds having the same formula and bonding arrangement but differing in the spatial arrangements of the atoms making them non super-imposable. It is well known that stereoisomers which exhibit different molecular configurations have different chemical properties. For instance, their unique and specific interaction with other molecules is suitable in various chemical [1, 2] and medicinal [3] applications. In contrast, the effect of steroisomerism on physical properties has been less studied. Regarding thermophysical properties, very few studies [4–7] were reported in literature until the recent works of Zeberg [8, 9]. These studies were focused on the influence of stereoisomerism on fluid density and fluid dynamic viscosity in wide ranges of pressure and temperature. Both studies concern the bicyclic naphthenic compound decahydronaphthalene which exists in the *cis*- and *trans*-configurations known as *cis*- and *trans*-decalin as shown in Fig. 1. In the thermodynamic [*P*, *T*] ranges investigated the *cis*-molecule appears as a denser fluid and its viscosity is significantly higher than the one of the *trans*-configuration. The most relevant of this work is certainly the significant increase of viscosity observed for *cis*-decalin at high pressures. These behaviours have been explained by the molecular structure which induces changes both in the molecular distance and free volume. In this context, it is worthwhile to question which the influence of stereoisomerism on static properties is. Up to date and to the best of our knowledge, any study was reported concerning the second derivatives of Gibbs potential. In the present work attention is still focused on the two stereoisomers *cis*- and *trans*-decalin. We propose a whole thermodynamic characterisation from acoustical and calorimetric measurements lead in extended thermodynamic [*P*, *T*] ranges. Thus, speed of sound was determined for the two stereo isomers in the temperature (303.15 to 373.15 K) and pressure range (0.1 to 150 MPa). Heat capacity measurements were carried out from atmospheric pressure to 60 MPa and at temperatures varying from 313.15 to 403.15 K. More-

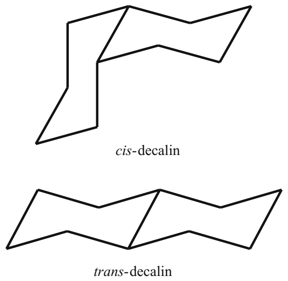

Fig. 1 Molecular structure of *cis*-decalin and *trans*-decalin

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over, density measurements required for the heat capacity determination were performed at high temperature (353. 15 to 403.15 K) to further data already available in literature [8]. On the basis of this experimental study, the objective of the present work is to provide an insight on the influence of stereoisomerism on some thermodynamic properties.

Experimental

Materials

The two chemicals used in this study are commercially available. *Cis*-decalin was from Merck with a chemical purity claimed to be>98% (Gas Chromatography). *Trans*-decalin was from Fluka with a chemical purity >99% (Gas Chromatography). The two chemicals were used without any further purification.

Calorimetric measurements

Heat capacity measurements C_P were performed with a Setaram C80 calorimeter adapted as a pressure scanning calorimeter [10]. Such devices allow the control of the whole set of thermodynamic variables pvT over wide ranges of pressure and temperature. Heat capacities were determined using the scanning method: a temperature variation at a constant rate, 0.15°C min^{-1} was induced under isobaric conditions and the calorimetric response was simultaneously recorded. As the calorimetric signal is proportional to the volumic heat capacity the determination of this quantity per mass unit entails the knowledge of density data, which were measured by means of an Anton–Paar 512P vibrating tube densimeter [11, 12]. The expected precision for a determination of C_P is about 0.5% based mainly on the estimated uncertainties in the calibration constant, ±0.3% and the calorimetric signal reproducibility ±0.2%. Detailed information about both the apparatus and the calibration procedure can be found elsewhere [13, 14].

Acoustic properties: speed of sound measurements

The measured quantity is the ultrasonic velocity. Such measurements were carried out using a pulse echo technique operating at 3 MHz. The apparatus, described previously in detail [15] is essentially made up of an autoclave cell closed at both ends by two identical plugs on which PZT piezoelectric elements are fixed. One acts as pulse transmitter/receiver whereas the second as a receiver only. The traveling time of the wave through the sample was determined from the measurement, by direct chronometry [16], of the first echo as well as the signal which has done a round trip in one of the plug by means of a numerical oscilloscope. The length of the sample path was determined precisely at each temperature and pressure condition by calibration with water [17, 18]. The uncertainty in the ultrasound velocity measured by this method was estimated taking into account the temperature and pressure effects on the path length to be about 0.2% over the entire P–T range. The high-pressure cell was immersed in a controlled and stirred liquid bath, which provides thermal stability of 0.02 K. Temperatures were measured using platinum probes (Pt100) embedded inside the cell and linked to high accuracy thermometer (AOIP brand). The uncertainty in the temperature measurements is estimated to be ±0.1 K. The pressure was generated by a high-pressure pneumatic pump and measured by a high-pressure transducer frequently checked *vs.* a dead mass tester to an accuracy of better than 0.02% full scale. It is convenient to note that ultrasonic velocity u has a thermodynamic meaningful if it coincides with the speed of sound c within the low frequency boundary and if the fluid remains in single phase state. When these conditions are satisfied the ultrasonic velocity u corresponds to a purely thermodynamic parameter linked to a reversible adiabatic process, and can be defined by the thermodynamic relationship:

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

in which κ_S is the isentropic compressibility and ρ is the density. The overall uncertainty has been estimated better than ±0.2% over the entire pressure-temperature range.

Results and discussion

Speed of sound (c) was determined for the two stereoisomers, namely *cis*- and *trans*-decalin from 303.15 to 373.15 K and from atmospheric pressure to 150 MPa. Experimental values are listed in Table 1. Heat capacities C_P of the two compounds were measured in wide ranges of pressure (0.1–70 MPa) and temperature (313.15–393.15 K). Comparisons of our C_P values with literature recommended data [19] available at the single atmospheric pressure shows Absolute Average Deviations AAD (%) of 0.16 and 0.8% for *cis*- and *trans*-decalin respectively. Such uncertainties largely remain within the experimental error of literature data which is claimed to be 1%. The raw data–massic heat capacities C_P (J K^{-1} kg^{-1}) – of the two compounds are reported in Table 2. Then, in the framework of Zabransky *et al.* [19], the $C_P(P,T)$ values for each compound at each pressure were fitted to a polynomial of the form:

$$C_P = \sum_{i=0}^{n} B_i \left(\frac{T}{100}\right)^{i} \tag{2}$$

Fits were performed using the Software Origin 7.0 with the final values of the coefficients B_i together with the absolute average deviation AAD (%) being listed in Table 3.

Thermodynamic consistency

Prior to analyze the effect of stereoisomerism on these derived properties, the thermodynamic consistency [14] between acoustic, calorimetric and volumetric properties was checked for each compound. Volumetric, acoustic and calorimetric data are linked by the following relationship:

$$\kappa_T = \kappa_S + \frac{T v_m \alpha_P^2}{C_{p,m}} \tag{3}$$

in which κ_T is the isothermal compressibility, κ_S is the isentropic compressibility, v_m is the molar volume, α_P is the isobaric thermal expansion coefficient and $C_{p,m}$ is the molar heat capacity.

Table 1 Experimental speed of sound values *c* (m s^{-1}) for *cis*-decalin and *trans*-decalin

T/K	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
P/MPa	*cis*-decalin								
0.1	1456.4	1415.2	1372.8	1331.0	1291.3	1253.1	1215.8	1179.2	1143.9
10	1502.3	1462.3	1420.4	1381.4	1344.7	1308.6	1272.8	1238.6	1205.0
20	1546.0	1506.5	1465.7	1429.3	1393.2	1358.8	1324.7	1291.3	1260.1
30	1585.9	1547.8	1508.9	1472.6	1438.4	1405.2	1372.6	1340.7	1310.8
40	1623.9	1587.4	1548.8	1514.5	1480.7	1448.6	1417.7	1386.9	1357.9
50	1661.0	1624.9	1587.5	1553.5	1521.4	1490.1	1459.9	1429.7	1401.2
60	1695.6	1663.0	1624.3	1591.0	1558.7	1529.3	1499.1	1470.4	1442.6
70	1729.0	1696.9	1658.9	1626.4	1595.1	1566.0	1536.8	1509.3	1482.2
80	1761.1	1730.0	1692.7	1660.6	1629.9	1601.4	1572.1	1545.4	1518.6
90	1792.1	1761.7	1724.6	1693.5	1663.4	1635.5	1607.6	1580.5	1555.3
100	1822.6	1792.5	1755.5	1725.3	1695.4	1668.1	1640.7	1614.1	1589.3
110	1851.4	1821.9	1785.6	1755.0	1726.1	1698.6	1672.3	1646.4	1621.7
120	1878.8	1850.2	1814.3	1784.3	1756.2	1729.1	1703.2	1677.3	1653.2
130	1906.6	1877.9	1842.2	1813.0	1784.7	1758.1	1732.3	1707.4	1683.4
140	1932.4	1905.1	1869.3	1841.9	1812.9	1786.6	1760.8	1736.5	1712.8
150	1958.2	1931.1	1895.8	1866.7	1839.8	1813.7	1788.4	1763.9	1741.3
	trans-decalin								
0.1	1398.4	1356.1	1316.2	1278.6	1238.7	1200.7	1165.2	1129.9	1094.6
10	1445.3	1406.5	1369.8	1331.9	1294.8	1260.1	1225.2	1191.7	1158.9
20	1492.5	1454.2	1416.8	1381.3	1345.9	1312.4	1280.0	1248.8	1217.7
30	1534.6	1497.2	1462.2	1427.7	1394.3	1361.8	1331.2	1300.7	1271.0
40	1574.3	1538.9	1504.7	1472.0	1439.0	1407.8	1377.8	1348.1	1320.6
50	1612.7	1578.3	1545.2	1512.5	1481.2	1450.8	1422.2	1394.0	1367.0
60	1649.4	1615.2	1579.6	1551.8	1520.7	1491.5	1463.2	1435.6	1409.1
70	1684.1	1650.6	1615.7	1588.6	1558.9	1530.2	1502.3	1476.0	1450.2
80	1718.0	1684.8	1650.3	1623.8	1594.8	1565.9	1540.0	1514.0	1488.6
90	1749.8	1717.7	1683.5	1658.0	1629.4	1601.5	1575.6	1550.1	1525.6
100	1781.1	1748.9	1715.7	1690.6	1662.4	1635.2	1609.7	1585.0	1560.6
110	1811.0	1779.8	1745.8	1721.6	1690.5	1667.5	1642.6	1617.9	1594.1
120	1839.6	1809.0	1775.5	1752.1	1719.7	1698.7	1674.2	1650.2	1626.6
130	1867.7	1837.5	1804.3	1781.0	1748.6	1728.9	1704.5	1680.8	1657.9
140	1894.6	1865.3	1832.2	1809.0	1778.5	1758.2	1734.0	1711.0	1688.1
150	1921.5	1891.8	1859.0	1837.0	1806.4	1785.9	1762.7	1739.4	1717.1

Table 2 Experimental massic heat capacity values C_P (J kg^{-1} K^{-1}) for *cis*-decalin and *trans*-decalin

P/MPa	0.1	20	40	60
T/K	*cis*-decalin			
313.15	1741.2	1733.7	1729.9	1740.2
323.15	1784.8	1776.3	1771.2	1782.4
333.15	1828.3	1819.5	1813.5	1825.2
343.15	1876.3	1863.5	1856.9	1868.4
353.15	1924.8	1908.3	1901.3	1912.1
363.15	1973.6	1953.7	1946.7	1956.2
373.15	2022.9	1999.9	1993.2	2000.8
383.15	2072.6	2046.8	2040.8	2046.0
393.15	2122.7	2094.4	2089.3	2091.5
	trans-decalin			
313.15	1711.7	1701.4	1700.1	1697.9
323.15	1755.4	1744.6	1740.1	1737.9
333.15	1800.5	1788.3	1780.8	1778.8
343.15	1846.9	1832.6	1822.2	1820.4
353.15	1894.6	1877.4	1864.4	1862.8
363.15	1943.6	1922.8	1907.3	1906.0
373.15	1994.0	1968.6	1951.0	1950.0
383.15	2045.7	2015.0	1995.4	1994.9
393.15	2098.7	2062.0	2040.5	2040.5

The integrated form of this equation allows to explicit the density, knowing the isentropic compressibility is linked to the speed of sound via Eq. (1):

$$\rho(p,T)=\rho(p_{\mathrm{ref}},T)+\int_{\mathrm{p_{ref}}}^{\mathrm{p}} c^{-2}\mathrm{d}p+\int_{\mathrm{p_{ref}}}^{\mathrm{p}}\frac{\alpha_{\mathrm{P}}^{2}}{C_{\mathrm{P}}}\mathrm{d}p \qquad (4)$$

In conditions compatible with the condensed liquid state, the third term in the right-hand of Eq. (4) has a minor contribution – largely inferior to 10% of the κ_T value – which decreases when pressure is increasing. In this term, the isobaric thermal expansion coefficient is obtained by numerical derivation.

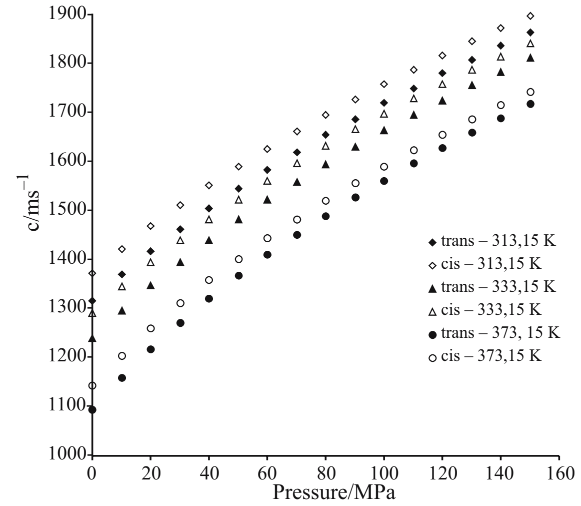

Fig. 2 Experimental speed of sound *c* (m s^{-1}) data as a function of pressure (isothermal curves) for *cis*-decalin (closed symbols) and *trans*-decalin (open symbols)

Hence, the expression (4) allows calculating high-pressure densities and isentropic compressibilities from ultrasonic measurements for a fluid provided that density as well as heat capacity at a reference pressure. Using this well-known methodology, largely detailed elsewhere [20], the estimation of density is fairly good, for instance deviation in the temperature range 303.15–373.15 K and up to 60 MPa of the estimated values if compared with the experimental ones [8] shows an AAD (%) of 0.05 and 0.12 for cis-decalin and for trans-decalin respectively. The validity of Eq. (1) is not systematic. For instance, at low temperature for which viscosity of *cis*-decalin is drastically increasing, one could speculate on its validity knowing that high viscosity could have induced dispersive effects. Thermodynamic consistency is then a methodology to check the reliability and the physical meaningful of each value. Moreover, it allows extending from 60 up to 100 MPa the estimation of density for each stereoisomer. The estimated densities and isentropic compressibilities for *cis*-decalin and *trans*-decalin are summarized in Tables 4 and 5.

Table 3 Coefficients B_i of Eq. (2) and Absolute Average Deviations AAD (%) of fit for molar heat capacities $C_P(PT)$ of *cis*- and *trans*-decalin

System	*P*/MPa	Parameters					
		B_1	B_2	B_3	B_4	B_5	AAD(%)
cis–decalin	0.1	221.86	–221.19	90.295	–15.822	1.0417	0.044
	20	6.5048	10.507	–2.5494	0.6062	–0.0436	0.004
	40	7.7824	10.739	–3.1289	0.7543	–0.0533	0.003
	60	221.86	–0.5585	2.5633	–0.4107	0.0291	0.010
trans–decalin	0.1	19.011	–2.2314	2.1726	–0.2039	0.0145	0.010
	20	24.494	–11.813	7.3335	–1.3018	0.0921	0.022
	40	–2.6835	21.391	–7.3444	1.5057	–0.1066	0.011
	60	13.269	3.1539	0.4575	0.0196	2E–10	0.001

Table 4 Density deduced ρ (kg m^{-3}) from ultrasonic measurements

T/K	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
P/MPa					*cis*-decalin				
0.1	896.80	889.09	881.49	873.93	866.39	858.79	851.10	843.27	835.24
10	902.58	895.13	887.82	880.58	873.39	866.18	858.91	851.55	844.03
20	908.07	900.84	893.77	886.80	879.90	873.02	866.11	859.13	852.03
30	913.25	906.21	899.35	892.61	885.96	879.35	872.74	866.08	859.34
40	918.17	911.29	904.61	898.07	891.64	885.26	878.90	872.52	866.08
50	922.86	916.13	909.60	903.23	896.98	890.81	884.68	878.54	872.35
60	927.36	920.74	914.34	908.13	902.04	896.05	890.11	884.18	878.23
70	931.67	925.16	918.88	912.79	906.86	901.02	895.25	889.51	883.76
80	935.82	929.40	923.23	917.26	911.45	905.76	900.14	894.56	888.99
90	939.83	933.48	927.40	921.54	915.84	910.28	904.80	899.37	893.95
100	943.70	937.42	931.42	925.65	920.06	914.61	909.25	903.96	898.69
110	947.45	941.23	935.30	929.61	924.12	918.77	913.52	908.35	903.21
120	951.09	944.92	939.06	933.44	928.03	922.77	917.63	912.57	907.55
130	954.63	948.51	942.69	937.14	931.80	926.63	921.58	916.62	911.71
140	958.07	951.99	946.22	940.73	935.46	930.36	925.40	920.53	915.73
150	961.43	955.37	949.65	944.21	939.00	933.97	929.09	924.31	919.60
					trans-decalin				
0.1	869.69	861.99	854.49	847.09	839.68	832.18	824.47	816.46	808.04
10	875.97	868.50	861.29	854.22	847.20	840.13	832.93	825.50	817.76
20	881.91	874.63	867.64	860.84	854.13	847.43	840.64	833.69	826.48
30	887.51	880.37	873.56	866.98	860.54	854.13	847.69	841.12	834.35
40	892.82	885.80	879.13	872.73	866.51	860.35	854.20	847.95	841.55
50	897.89	890.95	884.40	878.15	872.10	866.17	860.25	854.29	848.20
60	902.75	895.86	889.41	883.28	877.39	871.63	865.93	860.20	854.39
70	907.42	900.56	894.18	888.16	882.40	876.80	871.28	865.76	860.18
80	911.92	905.09	898.75	892.82	887.16	881.70	876.34	871.01	865.63
90	916.28	909.44	903.15	897.28	891.72	886.38	881.16	875.98	870.79
100	920.51	913.65	907.38	901.56	896.08	890.84	885.75	880.72	875.69
110	924.62	917.74	911.47	905.69	900.28	895.12	890.14	885.24	880.36
120	928.62	921.70	915.43	909.67	904.32	899.24	894.35	889.57	884.82
130	932.54	925.56	919.27	913.53	908.22	903.21	898.41	893.73	889.09
140	936.37	929.32	923.00	917.27	911.99	907.04	902.31	897.73	893.20
150	940.13	932.99	926.64	920.90	915.64	910.74	906.08	901.58	897.16

Effect of stereoisomerism on derived properties

The results of speed of sound measurements are plotted as a function of pressure (isothermal curves) in Fig. 2. The sets of speed of sound curves are regular and correspond to pressure coefficients $(\partial c/\partial P)_T$ and temperature coefficients $(\partial c/\partial T)_P$ which are positive and negative respectively. This quite classical behaviour is in agreement with the usual observations for simple liquid without any singularity. A comparison between the data of *cis* and *trans*-decalin reveals a systematic deviation (absolute average deviation AAD (%) between of the two sets of data of 2.58%). The speed of sound of *cis*-decalin is higher than the one of the *trans*-decalin in the experimental range covered up to 60 MPa (Fig. 2). Such difference is mainly due to volumetric effect. Indeed, as already observed [8] and emphasized by the present study performed at higher pressures and temperatures, the density of *cis*-decalin is also 2.5% higher than for *trans*-decalin. This higher density value of the *cis*-conformation was explained by its more twisted and less symmetrical molecular structure comparing to the more symmetrical and rigid *trans*-conformation.

Table 5 Isentropic compressibility κ_S (GPa^{-1}) deduced from ultrasonic measurements

T/K	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
P/MPa					*cis*-decalin				
0.1	0.524	0.563	0.603	0.646	0.693	0.742	0.795	0.852	0.914
10	0.490	0.523	0.558	0.595	0.634	0.675	0.719	0.766	0.817
20	0.460	0.489	0.520	0.552	0.586	0.621	0.658	0.698	0.740
30	0.435	0.461	0.488	0.516	0.545	0.576	0.608	0.642	0.678
40	0.412	0.436	0.460	0.485	0.511	0.538	0.566	0.596	0.627
50	0.392	0.414	0.436	0.458	0.482	0.506	0.531	0.557	0.584
60	0.375	0.394	0.414	0.435	0.456	0.477	0.500	0.523	0.547
70	0.359	0.377	0.395	0.414	0.433	0.453	0.473	0.494	0.515
80	0.344	0.361	0.378	0.395	0.413	0.431	0.449	0.468	0.487
90	0.331	0.347	0.362	0.378	0.394	0.411	0.428	0.445	0.463
100	0.319	0.334	0.348	0.363	0.378	0.393	0.409	0.424	0.441
110	0.308	0.322	0.335	0.349	0.363	0.377	0.391	0.406	0.421
120	0.298	0.311	0.323	0.336	0.349	0.362	0.376	0.389	0.403
130	0.288	0.300	0.312	0.324	0.337	0.349	0.361	0.374	0.387
140	0.280	0.291	0.302	0.314	0.325	0.337	0.348	0.360	0.372
150	0.272	0.282	0.293	0.304	0.314	0.325	0.336	0.347	0.358
					trans-decalin				
0.1	0.588	0.631	0.676	0.724	0.776	0.832	0.893	0.960	1.032
10	0.545	0.582	0.620	0.661	0.704	0.750	0.800	0.853	0.910
20	0.509	0.541	0.574	0.609	0.646	0.684	0.726	0.769	0.816
30	0.478	0.506	0.535	0.566	0.598	0.631	0.666	0.703	0.742
40	0.451	0.476	0.502	0.529	0.557	0.586	0.617	0.648	0.682
50	0.428	0.451	0.474	0.498	0.523	0.548	0.575	0.603	0.632
60	0.407	0.428	0.449	0.471	0.493	0.516	0.539	0.564	0.589
70	0.389	0.408	0.427	0.447	0.467	0.487	0.508	0.530	0.553
80	0.372	0.390	0.407	0.425	0.444	0.462	0.481	0.501	0.521
90	0.357	0.373	0.389	0.406	0.423	0.440	0.457	0.475	0.493
100	0.343	0.358	0.373	0.389	0.404	0.420	0.436	0.452	0.469
110	0.331	0.345	0.359	0.373	0.387	0.402	0.417	0.432	0.447
120	0.319	0.332	0.345	0.359	0.372	0.386	0.399	0.413	0.427
130	0.308	0.321	0.333	0.346	0.358	0.371	0.383	0.396	0.409
140	0.298	0.310	0.322	0.334	0.345	0.357	0.369	0.381	0.393
150	0.289	0.300	0.311	0.323	0.334	0.345	0.356	0.367	0.378

As it should be expected regarding the volumetric properties, speed of sound is higher for the denser fluid. It is convenient to note that speed of sound deviations between the two forms follow rigorously the same trends than for density. It decreases when pressure is increasing. The opposite behaviour is logically observed for the isentropic compressibility displayed in Fig. 3. From other part, the experimental heat capacity $C_P(P,T)$ curves, plotted as a function of temperature, are displayed in Fig. 4 for both the atmospheric and 60 MPa, the highest pressure employed here for heat capacity. In either case, a quite similar behaviour is observed with C_P which linearly increases with temperature. The effect of pressure is basically reduced the magnitude for *trans*-decalin. This effect of pressure is less marked for *cis*-decalin. It seems to pass through a minimum but such behaviour remains within the experimental error range. The difference between the two stereo-isomers could also be explained by the volumetric effect. This statement is better supported from an analysis of the different contribution to the total heat capacity. Ideal heat capacity C_P^0 data available in literature [7] shows very similar values for the two compounds. The absolute average

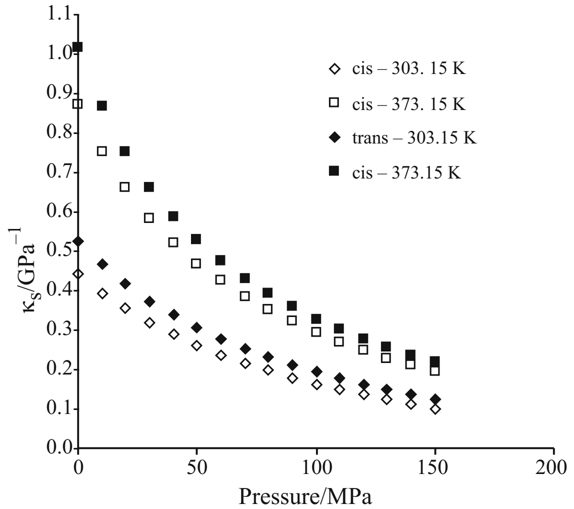

Fig. 3 Isentropic compressibility κ_S (GPa^{-1}) as a function of pressure (isothermal curves) for *cis*-decalin (closed symbols) and *trans*-decalin (open symbols)

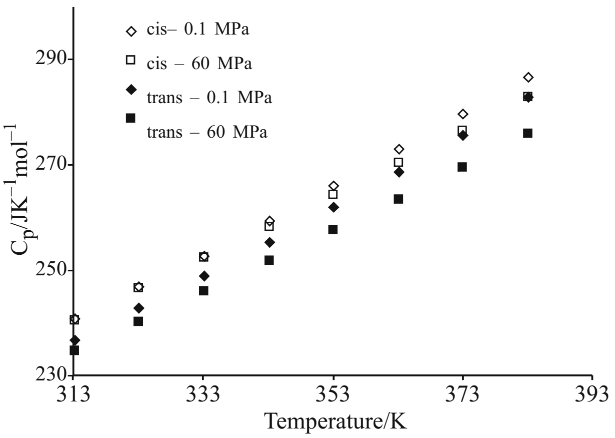

Fig. 4 Experimental molar heat capacities C_P (J K^{-1} mol^{-1}) as a function of temperature for *cis*-decalin (closed symbols) and *trans*-decalin (open symbols)

deviation between the two sets of data is inferior to 0.1%. Thus, the difference on the heat capacity results from the residual term as plotted in Fig. 5. Comprehensive studies [21, 22] devoted to the heat capacity behaviour *vs.* temperature from microscopic interactions have shown that in the case of non-associating compounds, the residual heat capacity is mainly governed by the free volume effect what is corroborated by the present study for the two stereoisomers.

Conclusions

Speed of sound, and heat capacities were measured for two stereoisomers, namely *cis*-decalin and *trans*-decalin in wide ranges of pressure and temperature. Some new measurements for density between 353.15 and 403.15 K are also provided. For these polycyclic naphthenic compounds both density, speed of sound and heat capacity have been found higher for the *cis* conformation than for the corresponding *trans* molecule. Thus, even if the present study is not enough to draw definitive and general conclusions, one can say the effect of stereoisomerism in static derived properties is not so marked as for dynamic properties. This effect can be analyzed as a direct consequence of volumetric effect due to the two molecular forms. Also, in first approximation, this experimental study seems to demonstrate that the intramolecular potential will not affect significantly the static properties.

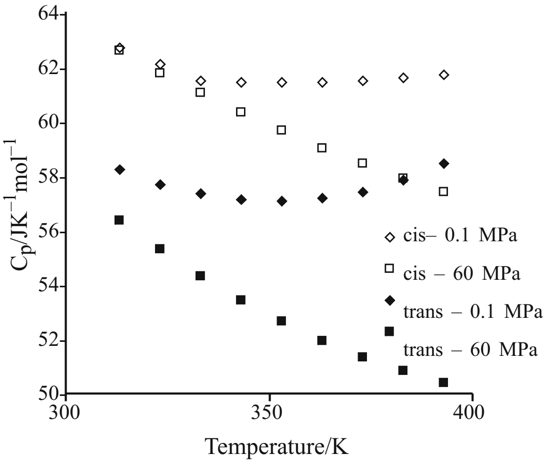

Fig. 5 Residual heat capacities $\Delta C_P(p,T)$ (J K^{-1} mol^{-1}) for *cis*-decalin (closed symbols) and *trans*-decalin (open symbols)

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