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Molar volume, thermal expansivity and isothermal compressibility of trans-decahydronaphthalene up to 200MPa and 446K

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The molar volume isotherms of trans-decahydronaphthalene ($C_{10}H_{18}$) between 293 and 446 K and at pressures from 10 to 200 MPa have been determined. A modified Tait equation of state is used to fit each experimental molar volume isotherm with a maximum average deviation of 0.029%. The thermal expansivity (cubic expansion coefficient) α and isothermal compressibility κ were determined by fitting the slopes of the isobaric curves and isotherms, respectively. The coefficients in the equation $V_m = C_1 + C_2T + C_3T^2 - C_4p - C_5pT$ have been fitted with an average deviation of 1.03%.

Keywords: trans-decahydronaphthalene, Tait equation, thermal expansivity, isothermal compressibility

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1. Introduction

Some substance could show special properties at high pressures,[1] so the studies on the properties of substance at high pressures are attracting increasing interest. The molar volume, thermal expansivity and isothermal compressibility at high pressures are important thermodynamic properties, because some other properties can be obtained from these data. The power of thermodynamics is that it allows immeasurable properties that are difficult to measure to be calculated from the measured properties. The easily measured properties most commonly used for these calculation are isobaric heat capacity (C_p), thermal expansivity (cubic expansion coefficient) α, and the isothermal compressibility, κ. These are state functions, and for pure substance are only a function of T, p. Both α and κ can be calculated from the equation of state $V = f(T, p)$, for the given (p, T) point.

Table 1. Melting-points T_m, boiling-points T_b, difference between T_b and T_m, and relative molecular masses m_r for some aromatic hydrocarbons and their fully hydrogenated counterparts.[3]

Name	Molecular formula	M_r/g·mol^{-1}	T_m/K	T_b/K	$T_b - T_m$/K
Benzene	C_6H_6	78.1	278.65	353.25	74.6
Cyclohexane	C_6H_{12}	84.2	279.65	354.15	74.5
Naphthalene	$C_{10}H_8$	128.2	354.15	491.15	136
trans-decahydronaphtalene	$C_{10}H_{18}$	138.3	240.60	460.7	220

Trans-decahydronaphthalene is an alicyclic analogue of naphthalene. It has potential to be used as a hydrogen source in hydrogen-oxygen fuel cell.[2] The melting-point and boiling-point of trans-decahydronaphthalene are lower than naphthalene.Normally, an increase in molar mass leads to an increase in both melting-point and boiling-point. However, in aromatic compounds, π-electron overlap stabilizes them relative to alicyclic analogues. In Refs.[4–8] some thermochemical data of trans-

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decahydronaphthalene have been reported, but we did not find any published values of experimental data at high pressures. This paper reports the pVT-data for trans-decahydronaphthalene between 293 and 446K and at pressures up to 20MPa. The thermal expansivity,α, and the isothermal compressibility, κ, are calculated.

2. Experiment

2.1. Material and its purity

The trans-decahydronaphthalene ($C_{10}H_{18}$, spectra grade, bp187.12°C) containing 1.10% of cis-decahydronaphthalene and 0.12% lighter components, was supplied by Merck Company (Darmstadt, Germany) and used without further purification, but was degassed for 2h at the temperature of 0°C and the pressure of 0.01MPa. The chromatographic analysis showed that it has a purity of 98.7%. The heat stability was investigated by heating for 4h at the temperature of 300°C. No new products were found.

2.2. Experimental apparatus and accuracy

The specific volume was determined from the amount of trans-decahydronaphthalene contained in a high pressure autoclave of known volume at given temperatures and pressures. The apparatus is similar to the equipment used earlier to determine high-pressure phase equilibria.[9] A schematic is shown in Fig.1. The cylindrical high-pressure autoclave (o.d 50mm, i.d 20mm, maximum internal volume 100cm^3) was made of stainless steel. A movable piston separates the contents of the autoclave from the pressure transmitting medium which drives the piston to generate high pressures inside the autoclave.

A sapphire window allows the observation of the contents of the autoclave. The window and the piston are each sealed by two O-rings (silicone rubber). The homogenization of temperatures was achieved by a magnetic stirring. The temperature of the autoclave was adjusted by a heating jacket and was measured with a calibrated chromel-alumel thermocouple inside the autoclave. A strain gauge precision transducer was used to measure the pressure. The pressure was manually generated by a screw-driven pump. The position of the piston and hence the volume of the samples were detected magnetically. A Hall-effect probe detected the position of the magnet which was fixed

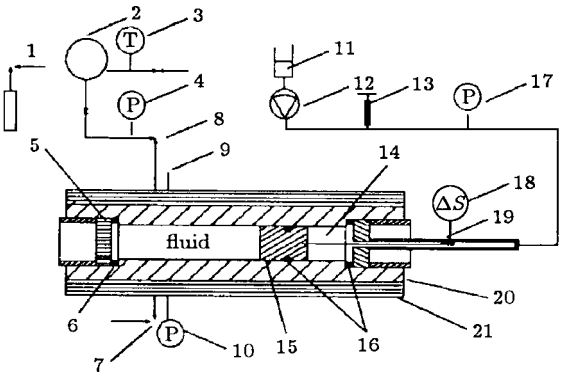


Fig.1. Schematic of experimental apparatus. 1. Small steel vessel; 2. glass bulb; 3. thermometer; 4. pressure sensor; 5. sapphire window; 6. O-ring; 7. valve; 8. capillary; 9. thermocouple; 10. pressure sensor; 11; oil-reservoir; 12. pump; 13. screw-driven pump; 14. oil; 15. piston; 16. O-ring; 17. pressure gauge; 18. Hall probe; 19. magnet; 20. autoclave; 21. heat jacket.

onto the end of the piston inside the autoclave. The Hall-effect probe was fixed on an electronic caliper (with an uncertainty of ±0.01mm) outside the autoclave. The electronic caliper was thus able to measure the position of the piston accurately.

The relationship between the effective autoclave volume and the position of the piston was calibrated by means of weighing water at different temperatures and pressures. The pressure-volume dependence, $\left(\frac{\mathrm{d}V}{\mathrm{d}p}\right)_T \frac{1}{V}$, was 2.060×10^{-5}MPa^{-1}. The temperature-volume dependence, $\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_p \frac{1}{V}$, was 4.050×10^{-5}K^{-1}. The uncertainties in temperature and pressure were ±0.5 K and ±0.1 MPa, respectively.

The mass of the added samples was weighed using an electronic balance with an accuracy of 0.0001g.

2.3. Procedure

Prior to its assembly and filling with sample, the equipment was carefully dried, evacuated and flushed with pure sample. After re-evacuation and weighing of the storage sample cylinder, the autoclave was then filled with the liquid sample. The amount of sample introduced was obtained by re-weighing of the cylinder. The content was initially compressed to several MPa with a screw driven pump before heating the autoclave. After the required temperature was reached, it was held for two hours to attain thermal equilibrium. Then the pressure was slowly adjusted to the starting value, and the variables of temperature, pressure and the position of piston were determined. The pressure was increased stepwise, and after the heat produced by compression had been levelled out, mea-

surements were carried out. Each experimental point on the isotherm was checked by making repeated measurements by increasing and decreasing the pressure three times. The densities and specific volumes were calculated from the volume of the autoclave, the mass of sample contained within it and the "dead volume" at room temperature. The calibrated autoclave volume must be modified by taking into account the thermal expansion, elastic deformation and possible plastic deformation. The maximum error associated with a specific volume measurement at 313.2K is ±0.2%. At elevated temperatures the maximum uncertainties are estimated to be ±0.4%. The laboratory temperature was maintained at 298K.

3. Results and discussion

Table 2 shows the molar volume of liquid trans-decahydronaphthalene relative to the measured values of temperature and pressure for six isotherms.

Table 2. Molar volume at different pressures for six isotherms.

p/MPa	V_m/cm^3·mol^{-1}					
	293.2K	300.2K	313.2K	333.2K	394.2K	446.2K
10	158.20	159.07	160.76	163.01	170.68	179.17
20	157.30	157.96	159.57	161.75	168.97	176.79
30	156.18	156.99	158.54	160.68	167.41	174.73
40	155.34	156.06	157.51	159.53	166.03	172.81
50	154.40	155.16	156.60	158.51	164.72	170.91
60	153.59	154.28	155.74	157.57	163.34	169.28
70	152.81	153.46	154.92	156.69	162.36	167.76
80	152.09	152.71	154.18	155.86	161.26	166.39
90	151.39	152.01	153.42	155.09	160.31	165.09
100	150.71	151.36	152.74	154.37	159.44	163.94
120	149.43	150.06	151.39	152.95	157.68	161.79
140	148.29	148.90	150.17	151.67	156.23	159.92
160	147.28	147.86	149.04	150.50	154.85	158.11
180	146.34	146.90	147.96	149.39	153.49	156.52
200	145.45	145.94	146.93	148.40	152.39	155.04

Different equations of state can be applied to describe the data. For fluids of high density, the modified Tait equation[10] is useful:

$$\frac{V_0 - V}{V_0} = A \ln\left(\frac{B + p}{B + p_0}\right). \qquad (1)$$

The equation is an isothermal equation and its form can be rewritten as:

$$V = V_0\left[1 - A \ln\left(\frac{B + p}{B + p_0}\right)\right]. \qquad (2)$$

Here, A and B are temperature-dependent constants and V_0 is the specific volume at a reference pressure p_0. In this paper, the modified Tait equation (2) is used to fit the experimental data. The parameters for trans-decahydronaphthalene (A, B,V_0 and p_0) for the modified Tait equation at the six selected temperatures along with the average and maximum deviations between experimental and calculated data are listed in Table 3.

Table 3. The parameters for trans-decahydronaphthalene (A, B,V_0 and p_0) used in the modified Tait equation along with the average and maximum deviations between experimental and calculated data.

T/K	V_0/cm^3·mol^{-1}	A	B/MPa	p_0/MPa	Av.Dev%[a)]	Max.Dev%[b)]
293.2	154.1042	0.0897	113.4399	53.6066	0.021	0.058
300.2	154.8045	0.0903	111.5337	53.6530	0.015	0.032
313.2	156.2998	0.0984	121.6723	53.7525	0.016	0.030
333.2	158.1599	0.0939	103.2662	53.8749	0.011	0.045
394.2	164.1374	0.0942	73.5475	54.2566	0.024	0.072
446.2	170.1492	0.1082	59.5585	54.5759	0.029	0.091

[a)] Av.Dev%= $\overline{\left|\frac{V_{\exp} - V_{\mathrm{calc}}}{V_{\exp}}\right| \times 100}$; [b)] Max.Dev= $\max\left(\left|\frac{V_{\exp} - V_{calc}}{V_{\exp}}\right| \times 100\right)$.

The molar volume values are related to their nominal isotherms by isobarically cross plotting the molar volume, V_m, against temperature and evaluating the thermal expansion and isothermal pressure expansion of the autoclave. In Fig.2, the data are shown in a p–V_m projection for the six isotherms.

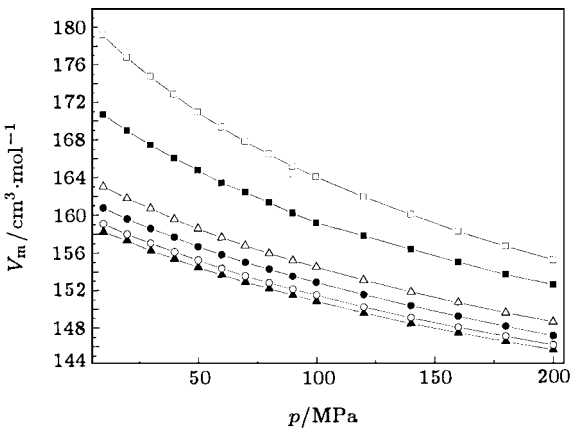


Fig.2. $p-V_m$ plots for the six isotherms: ▲, 293.2K; ◯, 300.2K; ●, 313.2K; △, 333.2K; ■, 394.2K; □, 446.2K.

From the experimental data the isobaric T-V_m curves can be obtained as shown in Fig.3. At constant pressure, the molar volume, V_m, is often written in the form:[11]

$$V_m = V_{m,0}(1 + at + bt^2), \tag{3}$$

where $V_{m,0}$ is the molar volume at 0°C and t is the temperatures in °C.

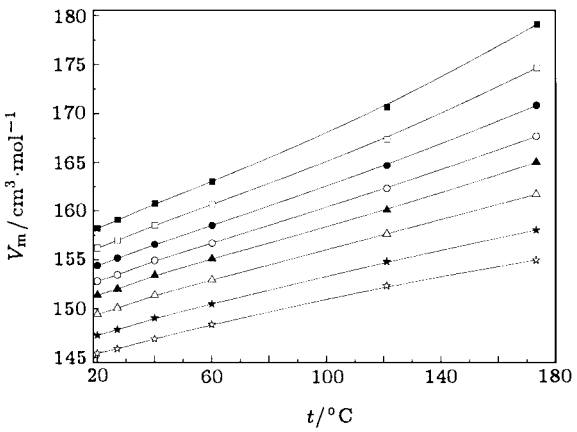


Fig.3. T versus V_m curves at constant pressures: ■, 10MPa; □, 30 MPa; ●, 50 MPa; ◯, 70 MPa; ▲, 90 MPa; △, 120 MPa; ★, 160 MPa; ☆, 200 MPa.

Table 4 presents the fitting results for different isobaric curves. It is found that the values of a and b are positive, and the values of $V_{m,0}$ decrease as the pressure is increased.

Table 4. The fitting results for different isobaric curves.

p/MPa	$V_{m,0}$/(cm^3/mol)	a/°C^{-1}	b/°C^{-2}	Av.Dev%[a)]	Max.Dev%[b)]
10	156.4154	6.0268×10^{-4}	1.3550×10^{-6}	0.099	0.252
20	155.4943	5.8083×10^{-4}	1.2016×10^{-6}	0.079	0.194
30	154.4552	5.9354×10^{-4}	9.3317×10^{-7}	0.098	0.254
40	153.6462	5.7686×10^{-4}	8.2407×10^{-7}	0.069	0.172
50	152.6715	5.9483×10^{-4}	5.3938×10^{-7}	0.064	0.159
60	151.9560	5.6994×10^{-4}	4.9668×10^{-7}	0.087	0.201
70	151.0713	5.9792×10^{-4}	2.2220×10^{-7}	0.064	0.177
80	150.4011	5.8747×10^{-4}	1.4246×10^{-7}	0.072	0.201
90	149.8035	5.9506×10^{-4}	-1.2313×10^{-7}	0.061	0.173
100	149.2422	6.025×10^{-4}	-1.4573×10^{-7}	0.057	0.172
120	147.7771	5.9308×10^{-4}	-2.7133×10^{-7}	0.058	0.167
140	146.6203	5.9798×10^{-4}	-4.3340×10^{-7}	0.040	0.140
160	145.6021	5.9695×10^{-4}	-5.8367×10^{-7}	0.023	0.093
180	144.7367	5.7120×10^{-4}	-5.8373×10^{-7}	0.012	0.048
200	143.7580	5.8640×10^{-4}	-7.6460×10^{-7}	0.019	0.046

[a)] $\text{Av.Dev\%} = \overline{\left|\frac{V_{exp} - V_{calc}}{V_{exp}}\right| \times 100}$;

[b)] $\text{Max.Dev} = \max\left(\left|\frac{V_{exp} - V_{calc}}{V_{exp}}\right| \times 100\right)$.

For most liquids and solids (especially non-polar organic substances) at higher temperatures and pressures, an approximate equation of state is

$$V_{\mathrm{m}} = C_1 + C_2T + C_3T^2 - C_4p - C_5pT, \qquad (4)$$

where C_1, C_2, C_3, C_4, C_5 are all positive constants that must be obtained from fitting the observed curves of V_{m} versus T and p. The term C_1 is much larger than each of the other terms. Table 5 lists the values of C_1 to C_5 which were obtained with a nonlinear least squares fitting procedure. In Table 6, the average deviation between measured and calculated values does not exceed 2.62%, thus, Eq.(4) provides a good description for the trans-decahydronaphthalene molar volume at high pressures and temperatures.

Table 5. The values of C_1 through C_5.

C_1 /cm^3·mol^{-1}	C_2 /cm^3·mol^{-1}·K^{-1}	C_3 /cm^3·mol^{-1}·K^{-2}	C_4 /cm^3·mol^{-1}·MPa^{-1}	C_5 /cm^3·mol^{-1}·MPa^{-1}·K^{-1}
124.4378	0.1127	1.0124×10^{-5}	2.3909×10^{-5}	2.0291×10^{-4}

Table 6. The deviation of V_{m} between measured and calculated values.

p/MPa	$d = \left\lvert \frac{V_{\mathrm{m,exp}} - V_{\mathrm{m,cal}}}{V_{\mathrm{m,exp}}} \right\rvert$ %						$\overline{d_{\mathrm{isobaric}}}$/%
	293.2K	300.2K	313.2K	333.2K	394.2K	446.2K	
10	0.28	0.31	0.41	0.35	0.61	0.18	0.36
20	0.08	0.01	0.067	0.01	0.07	1.05	0.21
30	0.25	0.24	0.18	0.26	0.38	0.40	0.28
40	0.41	0.44	0.35	0.55	0.73	0.18	0.45
50	0.64	0.63	0.61	0.77	1.05	0.77	0.75
60	0.78	0.81	0.76	0.95	1.41	1.20	0.98
70	0.90	0.95	0.88	1.08	1.53	1.58	1.15
80	0.99	1.05	0.95	1.19	1.73	1.87	1.29
90	1.06	1.11	1.04	1.25	1.95	2.12	1.42
100	1.13	1.15	1.07	1.29	2.12	2.29	1.51
120	1.19	1.21	1.13	1.34	2.01	2.53	1.57
140	1.17	1.18	1.11	1.31	1.93	2.60	1.55
160	1.06	1.07	1.02	1.19	1.80	2.62	1.46
180	0.89	0.90	0.90	1.04	1.66	2.51	1.32
200	0.69	0.73	0.74	0.80	1.35	2.32	1.10
$\overline{d_{\mathrm{isothermal}}}$/%	0.77	0.79	0.75	0.89	1.36	1.62	$\overline{d_{\mathrm{total}}} = 1.03\%$

Figure 4 shows the pressure–temperature curves for seven constant molar volume conditions. At constant molar volume, p can be expressed as

$$p = a + bT + cT^2, \qquad (5)$$

so we have

$$\left(\frac{\partial p}{\partial T}\right)_{V_{\mathrm{m}}} = b + 2cT, \qquad (6)$$

and

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_{V_{\mathrm{m}}} = 2c. \qquad (7)$$

The values of a, b, c are listed in Table 7. A polynomial fit of the data in Table 7 leads to the following expression for c : $c = 7791.91 - 151.44V_{\mathrm{m}} + 0.979V_{\mathrm{m}}^2 - 0.00211V_{\mathrm{m}}^3$.

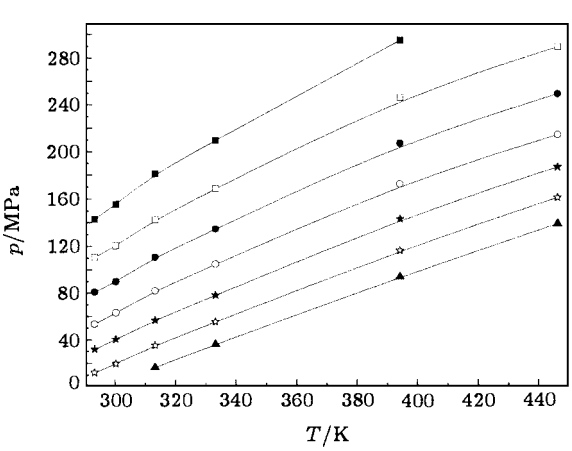


Fig.4. p Versus T curves at constant molar volumes: ■, 148cm^3·mol^{-1}; □, 150cm^3·mol^{-1}; ●, 152cm^3·mol^{-1}; ○,154cm^3·mol^{-1}; ★, 156cm^3·mol^{-1}; ☆, 158cm^3·mol^{-1}; ▲, 160cm^3·mol^{-1}.

Table 7. The Values of a, b, c.

V_m/(cm_3/mol)	a/MPa	b/(MPa / K)	c/(10^3MPa/K^2)
148	–662.94	3.6822	–3.1773
149	–649.51	3.6369	–3.0868
150	–631.43	3.4162	–3.0280
151	–623.08	3.3119	–2.9450
152	–583.50	3.0243	–2.5920
153	–560.49	2.8406	–2.3909
154	–539.30	2.6574	–2.1639
155	–498.16	2.382	–1.8287
156	–463.99	2.1358	–1.5163
157	–424.34	1.8709	–1.1874
158	–413.67	1.7654	–1.0687
159	–386.92	1.5762	–0.8349
160	–356.50	1.3777	–0.5983

The values of α and κ could be obtained from the definitions:

$$\alpha(T,p) = \frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_p, \tag{8}$$

$$\kappa(T,p) = -\frac{1}{V_m}\left(\frac{\partial Vm}{\partial p}\right)_T. \tag{9}$$

The values of α can be obtained from Eq.(8) at each constant pressure. In the same way, the values of κ at different pressures for each temperature can also be obtained using Eq.(9). The values of α and κ are displayed in Tables 8 and 9, respectively.

Table 8. The values of α at different temperatures and pressures.

p/MPa	$\alpha/10^4\mathrm{K}^{-1}$					
	293.2K	300.2K	313.2K	333.2K	394.2K	446.2K
10	6.4871	6.6438	6.9287	7.3511	8.5159	9.3597
20	6.2138	6.3520	6.6035	6.9769	8.0121	8.7693
30	6.2324	6.3335	6.5175	6.7906	7.5484	8.1055
40	6.0347	6.1203	6.2761	6.5075	7.1520	7.6289
50	6.0903	6.1386	6.2263	6.3564	6.7171	6.9832
60	5.8305	5.8751	5.9562	6.0767	6.4125	6.6620
70	5.9958	6.0013	6.0111	6.0249	6.0589	6.0788
80	5.8625	5.8581	5.8499	5.8369	5.7954	5.7579
90	5.6322	5.6279	5.6197	5.6068	5.5660	5.5295
100	5.4203	5.4178	5.4130	5.4054	5.3798	5.3555
120	5.7551	5.6947	5.5842	5.4182	4.9398	4.5615
140	5.7394	5.6568	5.5058	5.2791	4.6262	4.1090
160	5.6697	5.5670	5.3791	5.0972	4.2842	3.6379
180	5.4179	5.3170	5.1325	4.8553	4.0538	3.4145
200	5.4954	5.3691	5.1381	4.7911	3.7873	2.9840

The isobaric heat capacity of a substance $C_{p,m}$ is easily measured, but the isochoric heat capacity is hard to measure. From thermodynamics and the Maxwell relations, we have

$$C_{p,m} - C_{V,m} = TV_m\alpha^2/\kappa. \tag{10}$$

If the data for $C_{p,m}$ are available, the values of $C_{V,m}$ can be determined according to Eq.(10). In addition, calculations of $\left(\frac{\partial U}{\partial V}\right)_T$, $\left(\frac{\partial H}{\partial p}\right)_T$, $\left(\frac{\partial S}{\partial T}\right)_p$ and $\left(\frac{\partial S}{\partial p}\right)_p$, etc, can also be obtained from readily measured properties ($C_{p,m}$, α, κ).

Table 9. The values of κ at different temperatures and pressures.

p/MPa	$\kappa/10^5$MPa^{-1}					
	293.2K	300.2K	313.2K	333.2K	394.2K	446.2K
10	7.1890	6.3546	8.9585	11.5539	10.4412	18.9873
20	3.1685	3.1927	3.4446	3.8468	4.6974	6.4352
30	1.9800	2.0328	2.0847	2.2443	2.8612	3.6805
40	1.4051	1.4451	1.4612	1.5529	1.9532	2.4626
50	1.0664	1.0935	1.1025	1.1654	1.4116	1.7693
60	0.8438	0.8613	0.8700	0.9173	1.0522	1.3199
70	0.6870	0.6977	0.7078	0.7451	0.7966	1.0044
80	0.5711	0.5773	0.5890	0.6192	0.6059	0.7706
90	0.4825	0.4856	0.4987	0.5234	0.4583	0.5904
100	0.4128	0.4141	0.4284	0.4485	0.3408	0.4473
120	0.3114	0.3116	0.3272	0.3400	0.1663	0.2348
140	0.2424	0.2437	0.2597	0.2666	0.0434	0.0848
160	0.1937	0.1975	0.2133	0.2150	–0.0472	–0.0263
180	0.1585	0.1658	0.1808	0.1778	–0.1163	–0.1115
200	0.1327	0.1443	0.1581	0.1506	–0.1703	–0.1788

4. Conclusion

In this paper, the molar volume isotherms of trans-decahydronaphthalene ($C_{10}H_{18}$) between 293 and 446K and at pressures from 10 to 200MPa have been obtained. A modified Tait equation of state was used to fit each experimental molar volume isotherm with a maximum average deviation of 0.029%. The thermal expansivity (cubic expansion coefficient) α and isothermal compressibility κ were determined by fitting the slopes of the isobaric curves and isotherms, respectively.

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