Vol 18 No 9, September 2009
1674-1056/2009/18(09)/3795-07

Chinese Physics B

© 2009 Chin. Phys. Soc.
and IOP Publishing Ltd

Analysis of equation of state and thermodynamic functions for trans-decahydronaphthalene up to 200 MPa and 446 K*

Li Ming(李 明)[a)†], Chen Cui-Ling(陈翠玲)[b)], Sun Jiu-Xun(孙久勋)[c)], Tian Rong-Gang(田荣刚)[c)], and Xiao Jian-Rong(肖剑荣)[a)]

[a)] *Department of Mathematics and Physics, Guilin University of Technology, Guilin* 541004, *China*
[b)] *Department of Mathematics Science, Guangxi Normal University, Guilin* 541004, *China*
[c)] *Department of Applied Physics, University of Electronic Science and Technology, Chengdu* 610054, *China*

(Received 2 November 2008; revised manuscript received 12 December 2008)

This paper develops a modified Tait equation of state (EOS) for trans-decahydronaphthalene with four parameters A, B, V_0 and P_0 being treated as linear functions of temperature. The coefficients contained in these functions are determined through fitting the experimental compression data in the literature between 293 K and 446 K and at pressures from 10 to 200 MPa. Expressions for the thermal expansivity, isothermal compressibility and thermodynamic quantities are deduced and the numerical results are analytically derived. The numerical results show that the precision of the modified Tait EOS developed in this paper is superior to the EOS in the literature.

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

PACC: 0630N

1. Introduction

The equation of state (EOS) of a system describes the relationships between thermodynamic variables such as pressure, temperature and volume. It provides information on non-linear compression of a material at high pressure, and has been widely applied to engineering and other scientific research. Significant progress has been achieved over the past years to describe the properties of condensed matter in terms of universal relationships involving a small number of parameters. Especially, since Rose *et al*[1] proposed in 1986 that there exists a universal EOS (UEOS) valid for all types of solids through analysing the energy band data, a lot of forms of UEOS have been proposed with varying degrees of success.[2−6] Although these EOSs were proposed for solids originally, most of them have been applied to study the thermodynamic properties of liquids.[3−7] The traditional Tait EOS also has been used as a universal equation both for solids[8,9] and liquids.[10−16]

It has been shown that perturbation theories give fairly good descriptions of simple fluids.[17−21] However, perturbation theories are difficult to apply to complicated fluids since the intermolecular interaction is difficult to describe through simple functions. In these cases, the UEOS is preferable. The Vinet, KD, Baonza,[3−6] Tait[10−16] and Murnaghan[15,16] equations have been applied to different fluids. Recently, Adamenko *et al*[15,16] studied thermodynamic properties of C_{60} fullerene toluene and aqueous solutions through the Tait EOS. These works show that the modified Tait equation gives the best description for liquids with heavy molecules, and other more modern and complicated equations give poor descriptions.

Trans-decahydronaphthalene ($C_{10}H_{18}$) is an alicyclic analogue of naphthalene; its melting point and boiling point are lower than naphthalene. It has potential to be used as a hydrogen source in hydrogen-oxygen fuel cells.[22−26] Because thermodynamic data on trans-decahydronaphthalene is scarce,[27,28] Zhu *et al*[22] recently measured PVT data up to 200 MPa and 446 K. Although Zhu *et al* analysed their data with the aid of the Tait equation, they just determined parameters of the Tait equation along several isothermals, and could not determine the overall PVT

*Project supported by the Joint Fund of NSFC and CAEP (Grant No 10476007) and Program of Academic Excellence of Education Ministration of China (Grant No NCET-05-0799).
†Corresponding author. E-mail: liming@glite.edu.cn

relationship. Instead of the Tait equation, they alternatively developed the following PVT relationship:

$$V = C_1 + C_2T + C_3T^2 - C_4P - C_5PT. \quad (1)$$

Here the values of C_1 through C_5 are $124.4378\,\mathrm{cm^3{\cdot}mol^{-1}}$, $0.1127\,\mathrm{cm^3{\cdot}mol^{-1}{\cdot}K^{-1}}$, $1.0124\times10^{-5}\,\mathrm{cm^3{\cdot}mol^{-1}{\cdot}K^{-2}}$, $2.3909\times10^{-5}\,\mathrm{cm^3{\cdot}mol^{-1}{\cdot}MPa^{-1}}$, and $2.0291\times10^{-5}\,\mathrm{cm^3{\cdot}mol^{-1}{\cdot}MPa^{-1}{\cdot}K^{-1}}$, respectively. The precision of Eq.(1) is poor, and the compressibility calculated by Zhu *et al* even takes negative values at high pressure and high temperature regions. In terms of thermodynamics, the system would become unstable in such cases, and these negative values are physically unreasonable.

Based on the above analysis, it is necessary to construct a consistent PVT relationship for trans-decahydronaphthalene based on the experimental data available at present. Considering that trans-decahydronaphthalene is a macromolecular material, and the Tait equation has been shown to give a good description of complicated fluids,[10−16] we establish a new relationship for it on the basis of the Tait equation. In Section 2 of this paper, the analytic EOS is developed, and analytic expressions for thermal expansivity and compressibility are derived. Then we compare the numerical results with those of Ref.[22]. In Section 3, we derive the analytic expressions for thermodynamic functions, and give the numerical results.

2. Analysis of equation of state

The Tait EOSs in Refs.[10]–[16] are expressed in the following volume-analytic and pressure-analytic forms:

$$V = V_0\left[1 - A\ln\left(\frac{B+P}{B+P_0}\right)\right], \quad (2)$$

$$P = (P_0+B)\exp\left[\frac{1}{A}\left(1-\frac{V}{V_0}\right)\right] - B, \quad (3)$$

where V_0 is the volume at a reference pressure P_0. Originally, the Tait equation is isothermal, which means that four parameters A, B, V_0 and P_0 should be constant for every isothermal but they should take different values for different isothermals. In order to establish a consistent EOS, we take A, B, V_0 and P_0 as functions of temperature, and give their forms of functions as follows:

$$\begin{aligned} A &= A^0 + A'T, \\ B &= B^0 + B'T, \\ V_0 &= V_0^0 + V_0'T, \\ P_0 &= P_0^0 + P_0'T. \end{aligned} \quad (4)$$

Here the superscript '0' represents the values extrapolated to absolute zero degree, and the splash ' ′ ' denotes the derivatives with respect to temperature. It is easy to verify that Eq.(4) satisfies the PVT data of trans-decahydronaphthalene measured by Zhu *et al.* It should be pointed out that the modified EOS Eqs.(2) and (3) and thermodynamic functions derived in the following section with parameters in Eq.(4) are different from those of Adamenko *et al*,[15,16] and more general than them, for they just took B as a function of temperature in Refs.[15] and [16].

Equation (4) contains eight coefficients. In order to determine their values, we adopt the following procedures. At first, we determine their initial values by fitting A, B, V_0 and P_0 along six isothermals given by Zhu *et al.*[22] Then we adjust their values to minimize the average relative error of pressure — $N^{-1}\sum_i |(P_{i,\mathrm{cal}}/P_{i,\mathrm{exp}}) - 1|$, here N is the number of data points, and the final results are given by the following equations:

$$\begin{aligned} A &= 15.3 - 0.013T, \\ B &= 212 - 0.35T, \\ V_0 &= 123.7 + 0.1T, \\ P_0 &= 70 - 0.01T. \end{aligned} \quad (5)$$

Combining Eqs.(2), (3) and (5), we obtain a new EOS. In the following, we analyse its rationality through the comparison of our results and those of Zhu *et al.*[22]

Firstly, we compare the variations of A, B, V_0 and P_0 versus temperature from Eq.(5) with those given by Zhu *et al*,[22] and the results are listed in Fig.1. Evidently, the variations of four parameters from Eq.(5) are monotonous, but the variations of A and B given by Zhu *et al*[22] are not monotonous, which show that our optimized values are fairly different from the original ones. We think that the tendency of nonmonotonic variation is incorrect, and such an incorrect tendency is most probably just the reason that the compressibility incorrectly takes negative values for some data points given by Zhu *et al.*[22]

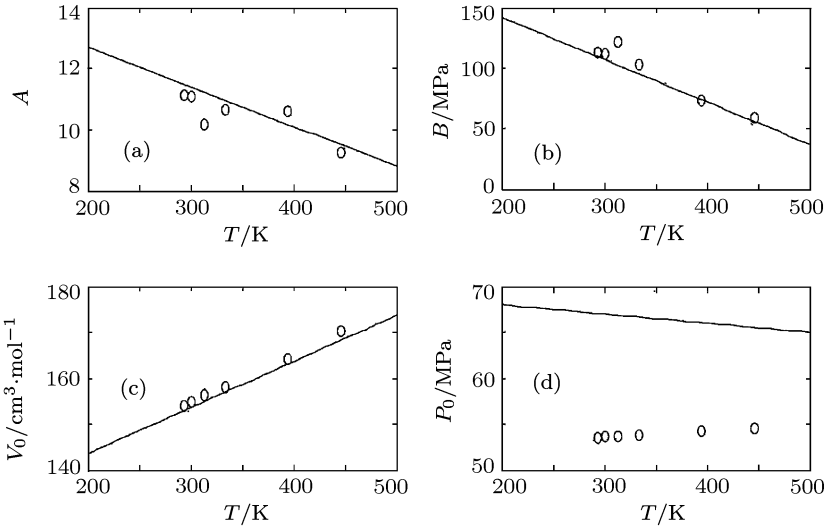


Fig.1. Dependences of parameters A, B, V_0 and P_0 on temperature respectively: circles, values given by Zhu *et al*;[22] lines, values calculated from Eq.(5) given in this paper.

Secondly, we compare eight isothermals calculated by Eqs.(3) and (5) with experimental data in Zhu *et al*,[22] and can see the results in Fig.2. The figure shows that the agreement of our EOS with experiment is fairly good. In order to quantitatively compare the precision of Eqs.(3), (5) and (1) of Zhu *et al*, we list the relative error of volume calculated according to the formula given in Table 1. Table 1 shows that for all data points our results are superior to those of Zhu *et al*. Their largest and average errors are 2.62% and 1.03%, but ours are 0.32% and 0.068%.

Table 1. Comparisons of relative errors of volume of Eq.(1) of Zhu *et al*[22] (represented by A) with those of Eqs.(3) and (5) (represented by B). The relative error of volume is defined by $\Delta V\% = \left|V_{i,\mathrm{cal}}/V_{i,\mathrm{exp}} - 1\right| \times 100\%$. $\overline{\Delta V_\mathrm{T}}\%$ is the average error along different isothermals, and $\overline{\Delta V_P}\%$ is the average error along different isobars.

T	293.2 K		300.2 K		313.2 K		333.2 K		394.2 K		446.2 K		$\overline{\Delta V_P}\%$	
P/MPa	A	B	A	B	A	B	A	B	A	B	A	B	A	B
10	0.28	0.013	0.31	0.006	0.41	0.056	0.35	0.104	0.61	0.220	0.18	0.006	0.36	0.068
20	0.08	0.095	0.01	0.006	0.07	0.044	0.01	0.08	0.07	0.320	1.05	0.079	0.21	0.104
30	0.25	0.013	0.24	0.006	0.18	0.082	0.26	0.006	0.38	0.287	0.40	0.155	0.28	0.092
40	0.41	0.064	0.44	0.038	0.35	0.063	0.55	0.038	0.73	0.235	0.18	0.174	0.45	0.102
50	0.64	0.013	0.63	0.032	0.61	0.083	0.77	0.038	1.05	0.212	0.77	0.094	0.75	0.079
60	0.78	0.020	0.81	0.006	0.76	0.096	0.95	0.032	1.41	0.300	1.20	0.077	0.98	0.089
70	0.90	0.007	0.95	0.02	0.88	0.097	1.08	0.026	1.53	0.197	1.58	0.048	1.15	0.066
80	0.99	0.007	1.05	0.026	0.95	0.123	1.19	0.019	1.73	0.211	1.87	0.036	1.29	0.070
90	1.06	0.000	1.11	0.02	1.04	0.111	1.25	0.000	1.95	0.175	2.12	0.012	1.42	0.053
100	1.13	0.020	1.15	0.013	1.07	0.124	1.29	0.019	2.12	0.125	2.29	0.03	1.51	0.055
120	1.19	0.067	1.21	0.047	1.13	0.092	1.34	0.000	2.01	0.14	2.53	0.025	1.57	0.062
140	1.17	0.081	1.18	0.06	1.11	0.073	1.31	0.007	1.80	0.026	2.62	0.006	1.55	0.056
160	1.06	0.068	1.07	0.054	1.02	0.047	1.19	0.007	1.80	0.026	2.62	0.006	1.46	0.035
180	0.89	0.062	0.90	0.048	0.90	0.007	1.04	0.027	1.66	0.059	2.51	0.019	1.32	0.037
200	0.69	0.062	0.73	0.082	0.74	0.054	0.80	0.02	1.35	0.02	2.32	0.045	1.10	0.047
$\overline{\Delta V_T}\%$	0.77	0.039	0.79	0.031	0.75	0.077	0.89	0.028	1.36	0.173	1.62	0.057	1.03	0.068

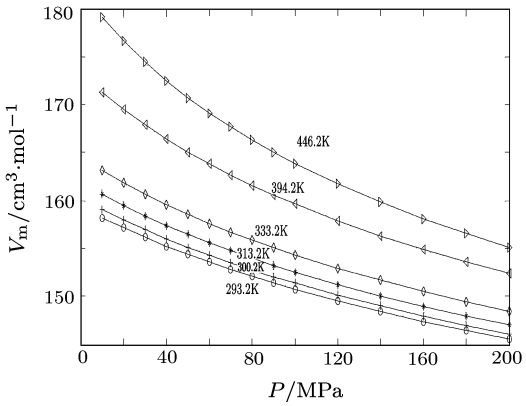


Fig.2. Variations of molar volume versus pressure at six temperatures: symbols are experimental data from Ref.[22]; lines are our numerical results.

Finally, we study thermal expansivity α and isothermal compressibility κ. From their definitions, we can derive

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{V_0'}{V} - \frac{1}{V}\left(A'V_0 + AV_0'\right)\ln\left(\frac{B+P}{B+P_0}\right) - \frac{AV_0}{V}\left(\frac{B'}{B+P} - \frac{B'+P_0'}{B+P_0}\right), \tag{6}$$

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{AV_0}{V\left(B+P\right)}. \tag{7}$$

According to Eqs.(6) and (7), the values of α and κ can be obtained. The values of α and κ are displayed in Tables 2 and 3, respectively. The comparisons of the $\alpha - p$ and $\kappa - p$ curves of our data and their data are shown in Figs.3 and 4.

Table 2. Values of α (in 10^{-4}K^{-1}) at different temperatures and pressures (in MPa).

P/MPa	293.2 K	300.2 K	313.2 K	333.2 K	394.2 K	446.2 K
10	7.6578	7.6723	7.7066	7.7809	8.2344	9.0937
20	7.3962	7.3992	7.4101	7.4426	7.7020	8.2411
30	7.1643	7.1576	7.1491	7.1472	7.2520	7.5517
40	6.9565	6.9417	6.9168	6.8861	6.8650	6.9779
50	6.7688	6.7469	6.7079	6.6526	6.5263	6.4895
60	6.5979	6.5698	6.5185	6.4420	6.2264	6.0661
70	6.4412	6.4077	6.3456	6.2505	5.9578	5.6937
80	6.2967	6.2584	6.1867	6.0751	5.7151	5.3621
90	6.1629	6.1202	6.0399	5.9136	5.4939	5.0636
100	6.0382	5.9916	5.9036	5.7640	5.2911	4.7927
120	5.8124	5.7589	5.6573	5.4946	4.9303	4.3166
140	5.6123	5.5529	5.4398	5.2577	4.6168	3.9084
160	5.4328	5.3683	5.2453	5.0464	4.3401	3.5516
180	5.2702	5.2013	5.0695	4.8558	4.0925	3.2347
200	5.1217	5.0488	4.9092	4.6824	3.8686	2.9497

Table 3. Values of κ (in 10^{-4}MPa^{-1}) at different temperatures and pressures (in MPa).

P/MPa	293.2 K	300.2 K	313.2 K	333.2 K	394.2 K	446.2 K
10	7.0515	7.2510	7.6460	8.3250	11.1360	15.0237
20	6.5509	6.7265	7.0731	7.6645	10.0575	13.2274
30	6.1195	6.2759	6.5835	7.1054	9.1785	11.8333
40	5.7438	5.8844	6.1602	6.6258	8.4476	10.7185
50	5.4135	5.5410	5.7904	6.2098	7.8299	9.8057
60	5.1208	5.2372	5.4645	5.8452	7.3007	9.0438
70	4.8595	4.9664	5.1749	5.5231	6.8420	8.3980
80	4.6248	4.7236	4.9159	5.2362	6.4404	7.8431
90	4.4127	4.5044	4.6828	4.9791	6.0857	7.3609
100	4.2201	4.3057	4.4718	4.7473	5.7701	6.9380
120	3.8834	3.9588	4.1047	4.3458	5.2325	6.2301
140	3.5988	3.6659	3.7958	4.0098	4.7913	5.6607
160	3.3548	3.4153	3.5322	3.7245	4.4223	5.1921
180	3.1433	3.1983	3.3046	3.4789	4.1090	4.7994
200	2.9581	3.0085	3.1058	3.2653	3.8395	4.4654

In Figs.3(a) and 3(b), we plot the variations in α versus pressure at six temperatures of two papers. Figure 3(a) is the result of Ref.[22], which shows that the variations are not smooth but are zigzag curves. Obviously, such curves are physically incorrect. Fig.3(b) is our result, from which we can see that the variations of α are smooth, and thus physically correct.

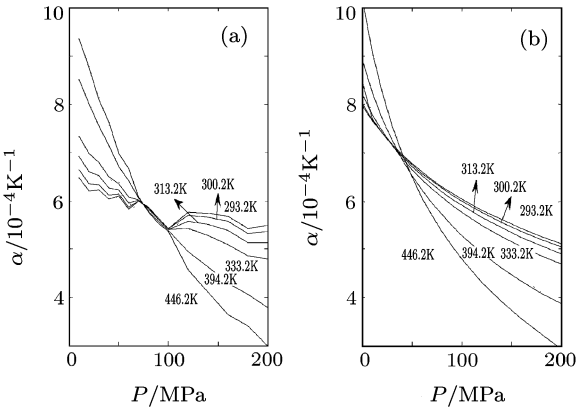


Fig.3. Dependences of thermal expansivity on pressure at six temperatures: the left subfigure gives the numerical results of Ref.[22]; the right subfigure contains the numerical results of our paper.

In Fig.4, the variations of κ versus pressure at six temperatures according to two papers are plotted, respectively. Figure 4(a) shows that the variations of Ref.[22] are dramatic and also not smooth. Even for pressure and temperature ranges higher than 150 MPa and 380 K, κ takes negative values. In terms of thermodynamics, a system with negative κ is unstable. So the tendency of Fig.4(a) is physically incorrect. However, Fig.4(b) shows that the κ calculated according to Eq.(7) always takes positive values correctly, and the variations are smoother and slower than those of Fig.4(a).

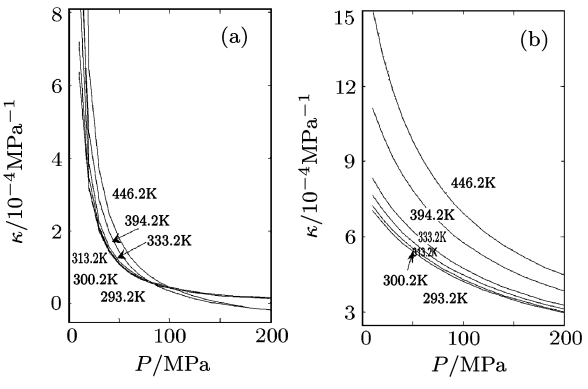


Fig.4. Dependences of thermal expansivity on pressure at six temperatures: the left subfigure gives the numerical results of Ref.[22]; the right subfigure contains the numerical results of our paper.

We believe that these results definitely verify that Eqs.(3) and (5) can provide a correct and good description of the PVT relationship for trans-decahydronaphthalene over wide ranges of pressure and temperature.

All the above results show that the new EOS is very rational and effective.

3. Analysis of thermodynamic functions

Although the four parameters A, B, V_0 and P_0 in Eqs.(5) are functions of temperature, we can derive analytical expressions for all thermodynamic quantities. In order to complete the task, we need the expression of isochoric heat capacity at zero pressure. The isobaric heat capacity C_P of a material is easily measured, but it is difficult to measure the isochoric heat capacity C_V. In order to get C_V, we use the following thermodynamic relationship:

$$C_P - C_V = TV\alpha^2/\kappa. \tag{8}$$

Once the EOS is available and α, κ is deduced, we can convert C_P to C_V. In Ref.[29], we find several values of C_P at zero pressure. By fitting the values of C_V converted from C_P, we obtain the following expression

$$C_V \equiv C_V^0 + C_V' T = -230.5478 + 1.4112T. \tag{9}$$

The formulas to evaluate internal energy and entropy by using the EOS are as follows:

$$U = \int C_V \mathrm{d}T + \int \left[T\left(\frac{\partial P}{\partial T}\right)_v - P \right] \mathrm{d}V + U_0, \tag{10}$$

$$S = \int \frac{C_V^0}{T}\mathrm{d}T + \int \left(\frac{\partial P}{\partial T}\right)_v \mathrm{d}V + S_0. \tag{11}$$

Considering that the integrals in Eqs.(10) and (11) are difficult to evaluate for the temperature dependence of parameters in Eq.(4), we firstly change Eqs.(10) and (11) to the following forms:

$$U = \int C_V \mathrm{d}T + T^2 \frac{\partial}{\partial T}\left[\frac{1}{T}\int P\mathrm{d}V\right] + U_0, \tag{12}$$

$$S = \int \frac{C_V^0}{T}\mathrm{d}T + \frac{\partial}{\partial T}\int P\mathrm{d}V + S_0. \tag{13}$$

Substituting Eq.(3) into Eqs.(12) and (13) and considering Eq.(4), we obtain

$$U = U_0 + C_V^0 T + (1/2)\, C_V' T^2 + AV_0(P_0 + B)\exp[A^{-1}(1 - V/V_0)] - \left[AV_0(P_0' + B') - A^{-1}A'V_0(P_0 + B) + (A'V_0 + AV_0')\,(P_0 + B)(1 + A^{-1}V/V_0)\right] \times T\exp[A^{-1}(1 - V/V_0)] + BV - B'TV, \tag{14}$$

$$S = S_0 + C_V^0 \ln T + C_V' T - \exp[A^{-1}(1 - V/V_0)][AV_0(P_0' + B') - A^{-1}A'V_0(P_0 + B) + (A'V_0 + AV_0')\,(P_0 + B)(1 + A^{-1}V/V_0)], \tag{15}$$

where U_0 and S_0 are integral constants. In the following calculations, we determine their values at the reference state ($T_{\rm ref} = 300$ K, $P_{\rm ref} = 0$), $U\,(T_{\rm ref},\ P_{\rm ref}) = 0$ and $S\,(T_{\rm ref},\ P_{\rm ref}) = 0$. If U and S are available, we can easily evaluate other thermodynamic functions. For example, the Helmholtz free energy is

$$F = U - TS = U_0 + TS_0 + C_V^0 T - C_V^0 T\ln T - (1/2)\, C_V' T^2 + AV_0(P_0 + B)\exp[A^{-1}(1 - V/V_0)] + BV - B'TV, \tag{16}$$

and the Gibbs free energy is

$$G = F + PV = U_0 + TS_0 + C_V^0 T - C_V^0 T\ln T - (1/2)\, C_V' T^2 + (AV_0 + V)\,(P_0 + B)\exp[A^{-1}(1 - V/V_0)] - B'TV. \tag{17}$$

In Fig.5, we plot the dependences of internal energy and entropy on molar volume at six temperatures. The figure shows that both quantities are an increasing function of temperature. But Fig.5(a) shows that the internal energy is also a decreasing function of volume, and Fig.5(b) shows that the variation of entropy is fairly slow and almost independent of volume.

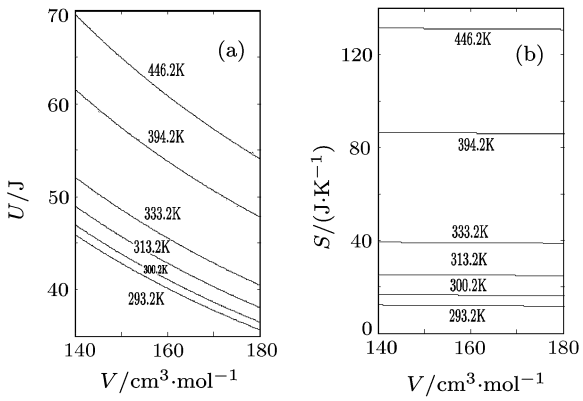


Fig.5. Dependences of internal energy and entropy on molar volume at six temperatures calculated in this paper.

4. Conclusion

In this paper, we put forward a modified Tait EOS for the trans-decahydronaphthalene. The four parameters A, B, V_0 and P_0 contained in the Tait EOS are taken as linear functions of temperature. Analytic expressions for the thermal expansivity, isothermal compressibility and thermodynamic properties are derived and the numerical results are presented. By introducing a novel fitting procedure, the coefficients contained in these functions are determined. All the numerical results indicate that the precision of the Tait EOS developed in this paper is superior to the EOS in the literature, and the new EOS overcomes the problem that the isothermal compressibility takes negative values for the EOS in the literature.

References

[1] Rose J H, Smith J R, Guinea F and Ferrante J 1984 *Phys. Rev.* B **29** 2963

[2] Vinet P, Smith J R, Ferrante J and Rose J H 1987 *Phys. Rev.* B **35** 1945

[3] Kuchhal P, Kumar R and Dass N 1997 *Phys. Rev.* B **55** 8042

[4] Schlosser H and Ferrante J 1989 *Phys. Rev.* B **40** 6405

[5] Baonza V G, Caceres M and Nunez J 1994 *Chem. Phys. Lett.* **228** 137

[6] Baonza V G, Caceres M and Nunez J 1994 *J. Phys. Chem.* **98** 4955

[7] Sun J X 2005 *J. Phys.: Condens. Matter* **17** L103
[8] Saxena S K 2004 *J. Phys. Chem. Solids* **65** 1561
[9] Shanker J, Singh B and Kushwah S S 1997 *Physica* B **229** 419
[10] Hartmann B, Lee G F, Balizer E and Acous J 2000 *Soc. Am.* **108** 65
[11] Chiang H H, Hieber C A and Wang K K 1991 *Polym. Eng. Sci.* **31** 116
[12] Zhang Y, Yuan Q and Yang J 2002 *Acta Polym. Sin.* **4** 467
[13] Liu J and Zhang Q J 2001 *Polym. Mater. Sci. Eng.* **17** 10
[14] Zhu T L and Wang M J 2002 *Polym. Mater. Sci. Eng.* **18** 89
[15] Adamenko I I, Bulavin L A and Moroz O K 2003 *J. Molec. Liq.* **105** 149
[16] Adamenko I I, Moroz K O and Prylutskyy Yu I 2005 *Int. J. Thermophys.* **26** 795
[17] Sun J X 2003 *Phys. Rev.* E **68** 061503
[18] Sun J X 2004 *Chem. Phys.* **302** 203
[19] Sun J X, Cai L C, Wu Q and Jing F Q 2003 *Physica* A **326** 482
[20] Sun J X 2005 *Canadian J. Phys.* **83** 55
[21] Chen Q F and Cai L C 2001 *Chin. Phys.* **10** 1144
[22] Zhu H G, Liu Z H and Tian Y L 2005 *Chin. Phys.* **14** 2433
[23] Lu S W 2005 *Chem. Phys. Commun.* **6** 47
[24] Mokbel I, Rauzy E and Loiseleur H 1995 *Fluid. Phase Equilib.* **108** 103
[25] Jiang S C and An L J 2003 *Macromol. Chem. Phys.* **204** 692
[26] Frezzotti D, Goffredi G and Bencini E 1995 *Thermochim. Acta* **265** 119
[27] Cox J D and Pilcher G 1970 *Thermochemistry of Organic and Organo-metallic Compounds* (New York: Academic)
[28] David R L 2003 *CRC Handbook of Chemistry and Physics* 83th edition (Boca Raton, FL: CRC Press)
[29] Domalski E S and Heariry E D 1996 *J. Phys. Chem. Ref. Data* **25** 1