

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

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Isobaric thermal expansivities, $\alpha_p(p, T)$, of seven binary mixtures of *n*-hexane with 1-hexanol (0.0553, 0.1088, 0.2737, 0.2983, 0.4962, 0.6036, and 0.7455 mol fraction of 1-hexanol) have been measured with a pressure-controlled scanning calorimeter over the pressure range from just above the saturation pressures to 350 MPa and at temperatures from 302.6 to 503.1 K. The low-temperature isotherms of α_p for particular mixtures observed with respect to the unique crossing point of *n*-hexane isotherms reveal an association effect which is reduced when the temperature increases. The high-temperature isotherms of α_p are very similar to the isotherms of pure *n*-hexane, especially for lower mole fractions of *n*-hexanol. No known equation of state can reproduce these properties.

KEY WORDS: 1-hexanol; *n*-hexane; high pressure, mixtures; pressure-controlled scanning calorimetry; thermal expansivities.

1. INTRODUCTION

The isobaric coefficient of thermal expansion, α_p , is an important thermodynamic property, even if it is a second cross derivative of the thermodynamic potential. Its present recognized importance stems from two major practical and theoretical points of view. First, recent developments

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of pressure-controlled scanning calorimeters make an easy determination possible with a reasonable precision over large ranges of pressure and temperature [1, 2]. Second, α_p is a property inherently related to the equation of state and, thus, can be conveniently explored in testing existing equations of state and in designing new ones. An important collection of $\alpha_p(p, T)$ data already exists for simple liquids. These data reveal that for simple liquids there always exists a unique crossing point of the isotherms of α_p , but the pressure at which it appears depends on the liquid under investigation [3]. Such a singular property has already been explored in the verification of equations of state for simple dense liquids [4] and in the creation of a new soft-sphere equation of state [5], which at the moment is the only equation of state approaching properly the crossing point of α_p isotherms for simple liquids, such as methane and even *n*-hexane. The pressure-temperature behavior of α_p for associated liquids is much more complex and depends very much on the nature of specific interactions. One possible approach for a better understanding of this behavior is a systematic investigation of similar liquids with distinct differences in specific interactions. We thought that a good example for such an approach could be the {*n*-hexane + 1-hexanol} system [6]. Until very recently, literature data on the pure *n*-alkanols and *n*-alkanes as well on the *n*-alkanes + *n*-alkanols binary mixtures were limited to near-atmospheric pressure and to a rather narrow temperature range [7]. In recent papers, we have reported detailed data for *n*-hexane [8] over the temperature range from 243 to 503 K at pressures up to 700 MPa and for 1-hexanol [9] over the temperature range from 303 to 503 K at pressures up to 400 MPa. In a correlation equation for $\alpha_p(p, T)$ of *n*-hexane, the data of Pruzan [10] were also included. In the present study we report measurements of $\alpha_p(p, T)$ for seven selected concentrations of binary mixtures of *n*-hexane + 1-hexanol at the temperatures 302.6, 352.6, 402.6, 452.7, and 503.0 K and at pressures up to 350 MPa.

2. EXPERIMENTAL PROCEDURE

Measurements of thermal expansivities were performed with a pressure-controlled scanning calorimeter described previously [2]. Here only basic principles of the experimental method are recalled. The calorimetric determination of the isobaric coefficient of thermal expansion is based on the Maxwell relation, which states that the isothermal pressure derivative of the entropy is equal with an opposite sign to the isobaric temperature derivative of the volume. When the pressure is scanned as a stepwise function of time at constant temperature, then from the pressure steps and

respective heat effects, the mean value, $\langle \alpha_{p,n} \rangle$, over the pressure step Δp_n is obtained through

$$\langle \alpha_{p,n} \rangle = \frac{kI_n}{\Delta p_n T} + \alpha_{p,ss} \quad (1)$$

where $I_n(V \cdot s)$ is the time integral of the calorimetric signal (heat-exchange rate) resulting from the calorimeter response to the pressure step Δp_n (MPa) performed under quasi-isothermal conditions, $\alpha_{p,ss}$ ($5.1 \cdot 10^{-5} \text{ K}^{-1}$) is the thermal expansivity of the stainless steel from which the calorimetric vessel is made, T (K) is the absolute temperature, and $k(\text{MPa} \cdot \text{V}^{-1} \cdot \text{s}^{-1})$ is a temperature-dependent calibration constant. Detailed reports on the values of the calibration constant at the respective temperatures, as well as on the procedures of calibration and on the verification of the results obtained against those produced by other techniques of determining α_p , are given in previous publications [2, 9, 11].

The 1-hexanol used in this study was Fluka 52830, with a purity of >99%; the *n*-hexane was Fluka 52765, with a purity of 99.5%. Both were used without further purification.

The mixtures were prepared by the weighing technique. To prevent sorption of moisture, the mixtures were transferred with a syringe into the calorimetric vessel immediately after preparation. The calorimetric vessel

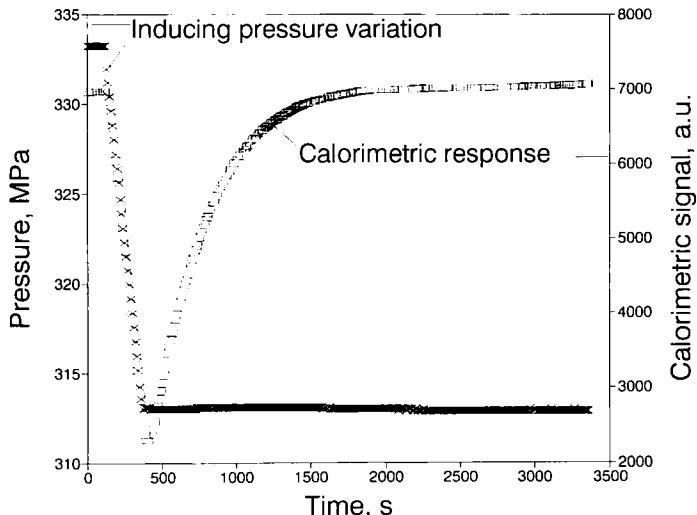


Fig. 1. Pressure-induced and Calorimetric Response Signals for the Determination of α_p for a {0.10881-hexanol-0.8912*n*-hexane} mixture at 503.1 K and 324.3 MPa.

was then rapidly closed with a cone and cone-retaining cap in such a way that no vapor space was present. After pressurizing to the highest pressure, the system was allowed to equilibrate both thermally and mechanically for a few hours before measurements began at a given temperature. Measurements were made with decreasing pressure. The rate of the pressure variations at each step was kept automatically constant at $0.078 \text{ MPa} \cdot \text{s}^{-1}$.

In Fig. 1, an example of both pressure-induced and calorimetric response signals is presented for the determination of α_p for a {0.1-hexanol + 0.9n-hexane} mixture at 503.1 K and 324.3 MPa.

3. RESULTS

Isobaric thermal expansivities measured at the temperatures 302.6, 352.6, 402.6, 452.8, and 503.1 K and at various pressures are given in Tables I–VII for the seven binary mixtures investigated: Table I for {0.05531-hexanol-0.9447n-hexane}, Table II for {0.10881-hexanol-0.8912n-hexane}, Table III for {0.27371-hexanol-0.7263n-hexane}, Table IV for {0.29831-hexanol-0.7017n-hexane}, Table V for {0.49621-hexanol-0.5038n-hexane}, Table VI for {0.60361-hexanol-0.3964n-hexane}, and Table VII for {0.74551-hexanol-0.2545n-hexane}. The pressures values in these tables are the mean pressures between the beginning and the end of the pressure steps. The end values were measured at the end of the thermogram recording the calorimetric signal, after thermal and mechanical equilibrium was reestablished. Each ending pressure became the beginning pressure for the next step. The accuracy limits given for $\langle \alpha_{p,n} \rangle$ are the estimated maximal errors obtained in combining the uncertainties on the measured pressures ($\pm 0.14 \text{ MPa}$), the integrals $I(\pm 0.2\%)$, the temperatures ($\pm 0.1\%$), $\alpha_{p,ss}(\pm 5\%)$, and the calibration constant k (from $\pm 0.8\%$ to $\pm 3\%$, depending on the temperature as reported in Ref. 9).

The experimental results were fitted by least squares to

$$\alpha_p(p, T) = [a(T)][p + b(T)]^{-0.5} \quad (2)$$

where $a(T)$ and $b(T)$ are functions of temperature:

$$a(T) = a_0 + a_1 T + a_2 T^2 \quad (3)$$

and

$$b(T) = b_0 + b_1 T + b_2 T^2 + b_3 T^3 \quad (4)$$

Table I. Results of Pressure-Controlled Scanning Calorimetric Measurements for the Isobaric Thermal Expansivities, α_p , of {0.0553 1-Hexanol–0.9447 *n*-Hexane} Mixture

<i>P</i> (MPa)	Δp (MPa)	<i>I</i> (V · s) ^a	α_p (10^{-4} K ⁻¹)
302.6 K			
344.6	19.9	−0.1078	5.06 ± 0.20
324.7	19.8	−0.1105	5.20 ± 0.20
304.9	19.7	−0.1135	5.34 ± 0.21
285.0	19.8	−0.1188	5.53 ± 0.21
265.1	19.8	−0.1218	5.68 ± 0.22
245.2	19.9	−0.1236	5.73 ± 0.22
225.3	19.8	−0.1287	5.97 ± 0.23
205.5	19.6	−0.1323	5.19 ± 0.24
185.6	20.2	−0.1421	6.42 ± 0.25
165.7	19.5	−0.1452	6.75 ± 0.26
145.9	19.7	−0.1545	7.07 ± 0.27
126.0	19.8	−0.1600	7.27 ± 0.28
106.1	19.6	−0.1713	7.83 ± 0.30
86.3	19.9	−0.1858	8.35 ± 0.32
66.4	19.8	−0.1988	8.93 ± 0.34
46.4	20.0	−0.2214	9.81 ± 0.37
31.2	10.1	−0.1275	11.06 ± 0.49
21.0	10.1	−0.1325	11.57 ± 0.51
10.9	10.0	−0.1455	12.71 ± 0.57
352.6 K			
345.0	20.0	−0.1141	4.64 ± 0.10
325.0	19.9	−0.1185	4.80 ± 0.10
305.0	19.8	−0.1226	4.97 ± 0.10
285.1	19.8	−0.1258	5.10 ± 0.10
265.3	19.7	−0.1276	5.19 ± 0.11
245.5	19.7	−0.1316	5.32 ± 0.11
225.7	19.8	−0.1395	5.59 ± 0.11
205.9	19.5	−0.1455	5.99 ± 0.12
186.2	19.9	−0.1572	6.21 ± 0.12
166.2	19.9	−0.1605	6.34 ± 0.13
146.9	19.8	−0.1690	6.66 ± 0.13
126.4	19.7	−0.1811	7.16 ± 0.14
106.5	19.9	−0.1969	7.63 ± 0.15
86.6	20.0	−0.2099	8.10 ± 0.16
66.6	19.8	−0.2308	8.91 ± 0.27
46.7	19.9	−0.2604	9.97 ± 0.19
31.6	10.0	−0.1491	11.24 ± 0.29
21.5	10.2	−0.1673	12.38 ± 0.31
11.3	10.1	−0.1859	13.85 ± 0.35

Table I. (*Continued*)

<i>P</i> (MPa)	<i>Δp</i> (MPa)	<i>I</i> (V · s) ^a	α_p (10^{-4} K^{-1})
402.6 K			
344.1	20.3	-0.1124	4.11 ± 0.09
323.8	20.1	-0.1169	4.27 ± 0.10
303.6	19.9	-0.1215	4.47 ± 0.10
283.7	19.7	-0.1261	4.65 ± 0.11
263.8	19.8	-0.1310	4.79 ± 0.11
243.8	20.0	-0.1374	4.97 ± 0.11
223.7	20.1	-0.1452	5.18 ± 0.11
203.6	19.8	-0.1528	5.50 ± 0.12
183.7	19.7	-0.1597	5.78 ± 0.13
163.8	20.1	-0.1682	5.95 ± 0.13
143.7	20.0	-0.1785	6.30 ± 0.14
123.8	19.6	-0.1944	6.95 ± 0.15
103.9	20.1	-0.2088	7.25 ± 0.15
83.8	10.0	-0.2286	7.91 ± 0.17
63.7	20.1	-0.2605	8.93 ± 0.19
43.5	20.0	-0.3047	10.39 ± 0.22
28.4	10.1	-0.1799	12.01 ± 0.32
18.3	9.9	-0.2021	13.71 ± 0.37
8.2	10.1	-0.2547	16.91 ± 0.45
452.8 K			
344.0	20.4	-0.1137	3.92 ± 0.10
323.5	20.3	-0.1152	3.97 ± 0.10
303.2	20.2	-0.1200	4.15 ± 0.11
282.9	20.1	-0.1254	4.33 ± 0.11
262.8	19.9	-0.1342	4.63 ± 0.12
242.8	20.0	-0.1383	4.74 ± 0.12
227.7	20.0	-0.1416	4.84 ± 0.12
202.6	19.9	-0.1469	5.03 ± 0.13
182.6	19.9	-0.1565	5.32 ± 0.13
162.6	19.8	-0.1666	5.65 ± 0.14
142.7	19.9	-0.1818	6.10 ± 0.15
122.8	19.8	-0.1965	6.58 ± 0.16
102.8	19.8	-0.2156	7.17 ± 0.17
82.9	20.0	-0.2437	7.96 ± 0.19
62.9	19.9	-0.2764	9.01 ± 0.21
42.8	20.1	-0.3340	10.67 ± 0.25
27.6	10.2	-0.2092	13.11 ± 0.39
17.4	10.1	-0.2921	15.90 ± 0.47

Table I. (Continued)

<i>P</i> (MPa)	Δp (MPa)	<i>I</i> (V · s) ^a	α_p (10^{-4} K^{-1})
503.1 K			
342.8	20.8	-0.1111	3.41 ± 0.11
322.0	20.6	-0.1142	3.76 ± 0.11
301.4	20.5	-0.1205	3.95 ± 0.12
280.9	20.3	-0.1268	4.17 ± 0.12
260.7	19.9	-0.1300	4.34 ± 0.13
240.5	20.1	-0.1360	4.48 ± 0.13
220.4	20.0	-0.1400	4.62 ± 0.14
200.4	20.0	-0.1518	4.97 ± 0.15
180.3	20.0	-0.1608	5.22 ± 0.15
160.3	19.9	-0.1675	5.44 ± 0.16
140.2	20.0	-0.1812	5.82 ± 0.17
120.2	19.8	-0.2030	6.52 ± 0.95
100.3	19.9	-0.2233	7.10 ± 0.05
80.3	20.0	-0.2519	7.88 ± 0.23
60.2	19.9	-0.2904	9.07 ± 0.26
40.2	20.1	-0.3685	11.28 ± 0.32
25.0	10.0	-0.2420	14.64 ± 0.51
15.0	10.1	-0.3285	19.52 ± 0.67

^a The integral of the calorimetric response to the quasi-isothermal pressure variation Δp .

Table II. Results of Pressure-Controlled Scanning Calorimetric Measurements for the Isobaric Thermal Expansivities, α_p , of {0.1088 1-Hexanol-0.8912 *n*-Hexane} Mixture

<i>P</i> (MPa)	Δp (MPa)	<i>I</i> (V · s)	α_p (10^{-4} K^{-1})
302.6 K			
344.2	19.9	-0.1049	4.94 ± 0.19
324.3	19.7	-0.1070	5.07 ± 0.20
304.6	19.6	-0.1102	5.23 ± 0.20
284.9	19.7	-0.1137	5.36 ± 0.21
265.2	19.6	-0.1163	5.50 ± 0.21
245.5	19.6	-0.1199	5.64 ± 0.22
225.8	19.6	-0.1270	5.96 ± 0.23
206.0	19.8	-0.1358	6.25 ± 0.24
186.2	19.7	-0.1385	6.42 ± 0.25
165.5	19.6	-0.1447	6.70 ± 0.26
146.7	19.7	-0.1523	6.98 ± 0.27
126.8	19.9	-0.1616	7.33 ± 0.28
106.8	19.9	-0.1718	7.76 ± 0.30
86.9	19.8	-0.1841	8.31 ± 0.32

Table II. (Continued)

<i>P</i> (MPa)	<i>Δp</i> (MPa)	<i>I</i> (V · s)	α_p (10^{-4} K^{-1})
67.1	19.8	-0.1984	8.91 ± 0.34
47.2	19.8	-0.2192	9.82 ± 0.37
32.3	9.9	-0.1200	10.68 ± 0.48
22.2	10.0	-0.1299	11.37 ± 0.51
12.2	10.0	-0.1384	12.10 ± 0.54
352.6 K			
343.6	20.1	-0.1151	4.63 ± 0.10
323.4	20.1	-0.1193	4.79 ± 0.10
303.3	19.9	-0.1225	4.94 ± 0.10
283.3	19.9	-0.1270	5.12 ± 0.10
263.3	19.7	-0.1321	5.34 ± 0.11
243.6	19.7	-0.1379	5.55 ± 0.11
223.7	19.9	-0.1449	5.76 ± 0.12
203.7	19.8	-0.1501	5.98 ± 0.12
183.8	20.0	-0.1562	6.15 ± 0.12
163.9	19.7	-0.1614	6.42 ± 0.13
144.0	19.8	-0.1738	6.86 ± 0.14
124.3	19.6	-0.1838	7.28 ± 0.14
104.5	19.9	-0.2003	7.76 ± 0.15
84.5	19.9	-0.2157	8.34 ± 0.16
64.5	19.9	-0.2360	9.05 ± 0.17
44.6	19.8	-0.2655	10.24 ± 0.19
29.6	10.0	-0.1518	11.44 ± 0.29
19.6	9.9	-0.1666	12.63 ± 0.32
9.6	9.9	-0.1868	14.08 ± 0.36
402.6 K			
343.4	20.2	-0.1205	4.38 ± 0.10
323.2	20.1	-0.1235	4.49 ± 0.10
303.0	19.9	-0.1260	4.61 ± 0.10
283.0	20.0	-0.1303	4.74 ± 0.11
263.8	19.8	-0.1354	4.94 ± 0.11
243.0	19.8	-0.1412	5.14 ± 0.11
223.1	20.0	-0.1510	5.42 ± 0.12
203.1	19.8	-0.1556	5.59 ± 0.12
183.2	19.9	-0.1620	5.79 ± 0.13
163.2	19.8	-0.1717	6.12 ± 0.13
143.3	19.8	-0.1840	6.55 ± 0.14
123.5	19.8	-0.1973	6.97 ± 0.15
103.6	19.7	-0.2144	7.55 ± 0.16
83.7	19.8	-0.2344	8.18 ± 0.17
63.8	19.8	-0.2344	9.05 ± 0.19
43.9	19.8	-0.3012	10.39 ± 0.22
28.9	10.1	-0.1755	11.76 ± 0.32

Table II. (Continued)

<i>P</i> (MPa)	<i>Δp</i> (MPa)	<i>I</i> (V · s)	α_p (10^{-4} K^{-1})
18.8	10.0	-0.2013	13.58 ± 0.37
8.7	9.9	-0.2447	16.46 ± 0.45
452.8 K			
343.4	20.3	-0.1157	3.99 ± 0.10
323.0	20.2	-0.1206	4.16 ± 0.11
302.7	20.2	-0.1274	4.37 ± 0.11
282.5	20.0	-0.1327	4.57 ± 0.12
262.5	19.9	-0.1361	4.69 ± 0.12
242.6	19.8	-0.1376	4.77 ± 0.12
222.6	20.0	-0.1454	4.97 ± 0.12
202.6	19.9	-0.1565	5.33 ± 0.13
182.6	19.9	-0.1565	5.64 ± 0.14
162.5	19.8	-0.1773	5.98 ± 0.15
142.6	19.9	-0.1852	6.21 ± 0.15
122.8	19.7	-0.1944	6.56 ± 0.16
102.9	20.0	-0.2140	7.07 ± 0.17
82.9	19.9	-0.2382	7.82 ± 0.19
63.0	19.8	-0.2718	8.89 ± 0.21
43.0	20.0	-0.3274	10.52 ± 0.25
27.8	10.1	-0.2000	12.64 ± 0.86
17.8	9.9	-0.2411	15.39 ± 0.46
7.8	10.0	-0.3422	21.37 ± 0.63
503.1 K			
342.5	20.6	-0.1124	3.70 ± 0.11
321.9	20.5	-0.1174	3.87 ± 0.12
301.4	20.2	-0.1232	4.09 ± 0.12
281.2	20.1	-0.1254	4.17 ± 0.12
261.1	19.9	-0.1300	4.34 ± 0.13
241.1	20.0	-0.1365	4.52 ± 0.13
221.0	19.9	-0.1430	4.72 ± 0.14
201.0	20.0	-0.1506	4.93 ± 0.15
181.0	19.9	-0.1621	5.28 ± 0.16
161.0	19.8	-0.1754	5.69 ± 0.17
141.1	19.8	-0.1876	6.07 ± 0.18
121.2	19.9	-0.2021	6.47 ± 0.19
101.2	20.1	-0.2203	6.94 ± 0.20
81.1	20.0	-0.2474	7.75 ± 0.22
61.0	20.0	-0.2942	9.15 ± 0.26
41.0	20.0	-0.3640	11.17 ± 0.32
25.9	10.0	-0.2365	14.33 ± 0.50
15.8	10.1	-0.3076	18.43 ± 0.64

Table III. Results of Pressure-Controlled Scanning Calorimetric Measurements for the Isobaric Thermal Expansivities, α_p , of {0.2737 1-Hexanol–0.7263 *n*-Hexane} Mixture

P (MPa)	Δp (MPa)	I (V · s)	α_p (10^{-4} K $^{-1}$)
302.6 K			
347.1	20.0	−0.1048	4.92 ± 0.19
327.1	19.9	−0.1069	5.02 ± 0.20
307.2	19.9	−0.1099	5.16 ± 0.20
287.3	19.8	−0.1132	5.32 ± 0.21
267.6	19.5	−0.1150	5.47 ± 0.21
247.9	19.7	−0.1198	5.60 ± 0.22
228.0	19.9	−0.1248	5.77 ± 0.22
208.1	19.8	−0.1290	5.98 ± 0.23
188.2	19.8	−0.1343	6.19 ± 0.24
168.3	19.8	−0.1399	6.44 ± 0.25
148.4	19.9	−0.1477	6.75 ± 0.26
128.4	19.9	−0.1551	7.05 ± 0.27
108.4	19.9	−0.1655	7.47 ± 0.29
88.4	19.9	−0.1772	7.98 ± 0.31
68.4	19.8	−0.1901	8.56 ± 0.33
48.5	19.9	−0.2081	9.31 ± 0.36
33.5	10.0	−0.1148	10.13 ± 0.45
23.5	10.0	−0.1204	10.67 ± 0.48
13.5	10.1	−0.1384	11.39 ± 0.51
352.6 K			
347.5	19.7	−0.1144	4.71 ± 0.10
327.8	19.7	−0.1177	4.83 ± 0.10
307.9	20.0	−0.1209	4.87 ± 0.10
287.7	20.1	−0.1252	5.01 ± 0.10
267.8	19.6	−0.1288	5.26 ± 0.11
248.1	19.6	−0.1347	5.47 ± 0.12
228.4	19.7	−0.1416	5.71 ± 0.12
208.6	19.7	−0.1466	5.88 ± 0.12
188.8	19.8	−0.1535	6.11 ± 0.12
168.9	19.8	−0.1604	6.35 ± 0.13
149.0	19.9	−0.1688	6.64 ± 0.13
129.0	19.9	−0.1799	7.03 ± 0.14
109.0	19.8	−0.1916	7.48 ± 0.15
89.1	19.7	−0.2055	7.97 ± 0.16
69.2	19.8	−0.2258	8.73 ± 0.17
49.2	19.9	−0.2510	9.63 ± 0.19
34.2	10.0	−0.1411	10.65 ± 0.27
24.2	9.9	−0.1505	11.49 ± 0.30
14.3	10.0	−0.1685	12.71 ± 0.32

Table III. (Continued)

<i>P</i> (MPa)	<i>Δp</i> (MPa)	<i>I</i> (V · s)	α_p (10^{-4} K^{-1})
402.6 K			
347.6	19.6	-0.1230	4.58 ± 0.11
328.1	19.4	-0.1252	4.70 ± 0.11
308.5	19.8	-0.1285	4.72 ± 0.11
288.7	19.7	-0.1287	4.74 ± 0.11
289.7	19.8	-0.1287	5.02 ± 0.11
249.0	20.0	-0.1436	5.17 ± 0.12
229.1	19.7	-0.1500	5.45 ± 0.12
209.3	19.6	-0.1586	5.75 ± 0.12
189.6	19.8	-0.1655	5.94 ± 0.13
169.8	19.7	-0.1747	6.25 ± 0.14
150.0	19.7	-0.1852	6.59 ± 0.14
130.1	19.8	-0.1965	6.94 ± 0.15
110.1	19.9	-0.2117	7.39 ± 0.16
90.1	19.9	-0.2299	8.01 ± 0.17
70.2	19.8	-0.2537	8.81 ± 0.19
50.2	20.0	-0.2896	9.91 ± 0.21
35.2	10.0	-0.1635	11.09 ± 0.30
25.1	9.9	-0.1815	12.37 ± 0.34
15.1	9.9	-0.2054	13.96 ± 0.38
452.8 K			
347.4	20.0	-0.1150	4.02 ± 0.10
327.2	20.1	-0.1202	4.17 ± 0.11
307.2	19.8	-0.1266	4.42 ± 0.11
287.4	19.7	-0.1320	4.62 ± 0.12
267.6	19.8	-0.1374	4.75 ± 0.12
247.9	19.5	-0.1428	5.00 ± 0.13
228.3	19.7	-0.1508	5.20 ± 0.13
208.5	19.6	-0.1581	5.44 ± 0.14
188.8	19.8	-0.1673	5.69 ± 0.14
169.0	19.7	-0.1775	6.02 ± 0.15
149.1	19.9	-0.1896	6.35 ± 0.16
129.1	19.9	-0.2021	6.71 ± 0.16
109.1	19.9	-0.2189	7.22 ± 0.18
89.0	20.0	-0.2371	7.76 ± 0.19
69.0	19.9	-0.2682	8.74 ± 0.21
49.0	19.9	-0.3116	10.11 ± 0.24
34.0	10.0	-0.1862	11.87 ± 0.36
23.9	10.0	-0.2158	13.65 ± 0.41
13.8	10.1	-0.2291	16.21 ± 0.48

Table III. (Continued)

P (MPa)	Δp (MPa)	I (V · s)	α_p (10^{-4} K^{-1})
503.1 K			
347.4	20.1	-0.1175	3.94 ± 0.12
327.0	20.4	-0.1210	3.99 ± 0.12
307.2	19.1	-0.1259	4.15 ± 0.13
287.6	19.8	-0.1267	4.26 ± 0.13
267.9	19.5	-0.1349	4.84 ± 0.14
248.3	19.5	-0.1411	4.75 ± 0.14
228.4	20.0	-0.1482	4.85 ± 0.14
208.5	19.7	-0.1519	5.02 ± 0.15
188.6	19.7	-0.1630	5.35 ± 0.16
168.8	19.8	-0.1699	5.54 ± 0.16
149.0	19.7	-0.1823	5.93 ± 0.17
129.0	19.9	-0.1965	6.29 ± 0.18
109.0	19.8	-0.2148	6.86 ± 0.20
89.1	20.0	-0.2402	7.56 ± 0.22
69.1	19.7	-0.2720	8.59 ± 0.25
49.2	19.9	-0.3276	10.16 ± 0.29
34.2	10.1	-0.2000	12.09 ± 0.42
24.0	10.0	-0.2403	14.58 ± 0.51
14.0	10.1	-0.3165	18.97 ± 0.66

Table IV. Results of Pressure-Controlled Scanning Calorimetric Measurements for the Isobaric Thermal Expansivities, α_p , of {0.2983 1-Hexanol-0.7017 *n*-Hexane} Mixture

P (MPa)	Δp (MPa)	I (V · s)	α_p (10^{-4} K^{-1})
302.6 K			
342.9	19.9	-0.1035	4.88 ± 0.19
322.9	20.0	-0.1078	5.02 ± 0.20
302.9	19.8	-0.1101	5.17 ± 0.20
282.9	19.9	-0.1131	5.29 ± 0.21
263.0	19.8	-0.1160	5.43 ± 0.21
243.1	19.7	-0.1202	5.62 ± 0.22
223.3	19.8	-0.1245	5.79 ± 0.22
203.4	19.8	-0.1292	5.97 ± 0.23
183.4	19.9	-0.1352	6.22 ± 0.24
163.5	19.8	-0.1404	6.46 ± 0.25
143.5	19.9	-0.1483	6.77 ± 0.26
123.6	19.8	-0.1566	7.15 ± 0.28
103.7	19.8	-0.1654	7.50 ± 0.29
83.7	20.0	-0.1788	8.01 ± 0.31

Table IV. (Continued)

<i>P</i> (MPa)	<i>Ap</i> (MPa)	<i>I</i> (V · s)	α_p (10^{-4} K $^{-1}$)
63.6	19.9	-0.1919	8.62 ± 0.33
43.6	20.1	-0.2129	9.40 ± 0.36
28.5	9.9	-0.1181	10.81 ± 0.47
18.5	9.9	-0.1236	11.03 ± 0.50
8.6	9.9	-0.1341	11.84 ± 0.53
352.6 K			
343.2	20.0	-0.1175	4.76 ± 0.10
323.2	19.9	-0.1197	4.85 ± 0.10
303.2	19.8	-0.1226	4.97 ± 0.10
283.2	20.0	-0.1277	5.12 ± 0.11
263.3	19.7	-0.1307	5.30 ± 0.11
243.5	19.8	-0.1352	5.45 ± 0.11
223.6	19.8	-0.1418	5.68 ± 0.12
203.7	19.8	-0.1470	5.86 ± 0.12
183.7	19.9	-0.1540	6.10 ± 0.12
163.9	19.8	-0.1607	6.38 ± 0.13
144.0	19.9	-0.1710	6.72 ± 0.13
124.1	19.8	-0.1810	7.11 ± 0.14
104.1	19.8	-0.1929	7.52 ± 0.15
84.2	19.9	-0.2101	8.13 ± 0.16
64.2	19.8	-0.2301	8.88 ± 0.17
44.3	19.9	-0.2575	9.86 ± 0.19
29.3	10.0	-0.1472	11.09 ± 0.28
19.3	9.8	-0.1564	12.00 ± 0.31
9.3	9.9	-0.1754	13.25 ± 0.34
402.6 K			
342.8	19.8	-0.1239	4.57 ± 0.11
322.9	19.9	-0.1276	4.67 ± 0.11
302.9	19.9	-0.1318	4.79 ± 0.11
282.9	19.9	-0.1357	4.94 ± 0.11
263.0	19.8	-0.1404	5.10 ± 0.12
243.1	19.8	-0.1463	5.31 ± 0.12
223.2	19.9	-0.1525	5.48 ± 0.12
203.3	19.9	-0.1595	5.71 ± 0.13
183.3	19.9	-0.1680	5.98 ± 0.13
163.3	19.8	-0.1769	6.29 ± 0.14
143.4	20.0	-0.1882	6.62 ± 0.14
123.5	19.8	-0.1989	7.03 ± 0.15
103.5	19.9	-0.2137	7.46 ± 0.16
83.5	19.9	-0.2359	8.19 ± 0.18
63.5	19.9	-0.2653	9.13 ± 0.19
43.5	19.9	-0.3027	10.39 ± 0.22

Table IV. (Continued)

<i>P</i> (MPa)	<i>Ap</i> (MPa)	<i>I</i> (V · s)	α_p (10^{-4} K^{-1})
28.4	10.1	-0.1779	11.89 ± 0.32
18.3	9.9	-0.1978	13.42 ± 0.37
8.3	9.9	-0.2345	15.80 ± 0.43
452.8 K			
342.1	19.9	-0.1225	4.26 ± 0.11
322.1	20.0	-0.1281	4.43 ± 0.11
302.2	19.9	-0.1316	4.54 ± 0.12
282.0	20.0	-0.1356	4.66 ± 0.12
262.0	19.8	-0.1404	4.84 ± 0.12
242.1	19.8	-0.1456	5.02 ± 0.13
222.2	19.8	-0.1521	5.20 ± 0.13
202.3	20.0	-0.1608	5.44 ± 0.14
182.3	19.9	-0.1701	5.73 ± 0.14
162.3	19.9	-0.1990	6.01 ± 0.15
142.3	19.9	-0.1912	6.38 ± 0.16
122.3	19.8	-0.2048	6.84 ± 0.17
102.3	20.0	-0.2223	7.32 ± 0.18
82.3	20.0	-0.2491	8.12 ± 0.20
62.2	20.0	-0.2825	9.17 ± 0.22
42.2	19.9	-0.3358	10.54 ± 0.26
27.1	10.1	-0.2052	12.89 ± 0.39
16.9	10.1	-0.2473	15.53 ± 0.46
503.1 K			
341.1	20.1	-0.1181	3.96 ± 0.12
320.9	20.0	-0.1241	4.15 ± 0.13
300.9	19.9	-0.1284	4.29 ± 0.13
280.9	19.9	-0.1310	4.38 ± 0.13
261.0	19.7	-0.1360	4.55 ± 0.14
241.1	19.9	-0.1435	4.74 ± 0.14
221.2	19.8	-0.1496	4.95 ± 0.15
201.3	19.9	-0.1585	5.19 ± 0.15
181.3	19.9	-0.1666	5.42 ± 0.16
161.4	19.8	-0.1770	6.14 ± 0.17
141.4	19.9	-0.1909	6.14 ± 0.18
121.5	19.8	-0.2038	6.54 ± 0.19
101.6	19.9	-0.2246	7.14 ± 0.21
81.6	20.0	-0.2518	7.89 ± 0.23
61.6	19.8	-0.2908	9.1 ± 0.26
41.6	19.9	-0.3584	11.09 ± 0.32
26.6	10.0	-0.2286	13.86 ± 0.48
16.5	10.0	-0.2936	17.80 ± 0.66

Table V. Results of Pressure-Controlled Scanning Calorimetric Measurements for the Isobaric Thermal Expansivities, α_p , of {0.4952 1-Hexanol–0.5038 *n*-Hexane} Mixture

<i>P</i> (MPa)	Δp (MPa)	<i>I</i> (V · s)	α_p (10^{-4} K $^{-1}$)
302.6 K			
343.9	20.1	−0.1027	4.80 ± 0.19
323.4	20.2	−0.1071	4.96 ± 0.19
303.3	19.8	−0.1041	4.92 ± 0.29
283.4	19.8	−0.1103	5.19 ± 0.20
263.7	19.6	−0.1140	5.40 ± 0.21
243.9	19.7	−0.1186	5.55 ± 0.22
224.2	19.5	−0.1205	5.70 ± 0.22
204.6	19.7	−0.1244	5.80 ± 0.23
184.7	19.8	−0.1297	6.01 ± 0.23
164.8	19.8	−0.1347	6.22 ± 0.24
145.0	19.8	−0.1411	6.50 ± 0.25
125.1	19.8	−0.1490	6.82 ± 0.26
105.3	19.7	−0.1573	7.20 ± 0.28
85.4	19.8	−0.1681	7.65 ± 0.29
65.5	19.8	−0.1808	8.16 ± 0.31
45.6	19.9	−0.1980	8.87 ± 0.34
30.6	9.9	−0.1083	9.68 ± 0.43
20.5	10.3	−0.1186	10.19 ± 0.45
10.3	9.9	−0.1255	10.85 ± 0.49
352.6 K			
343.5	20.1	−0.1133	4.58 ± 0.10
323.3	20.0	−0.1171	4.73 ± 0.10
303.3	19.9	−0.1204	4.87 ± 0.10
283.3	19.9	−0.1241	5.02 ± 0.11
263.4	19.7	−0.1265	5.14 ± 0.11
243.6	19.8	−0.1318	5.33 ± 0.11
223.7	19.9	−0.1376	5.49 ± 0.11
203.7	19.8	−0.1431	5.72 ± 0.12
183.7	20.0	−0.1505	5.94 ± 0.12
163.7	19.8	−0.1570	6.22 ± 0.13
143.7	19.9	−0.1656	6.52 ± 0.13
122.8	19.8	−0.1746	6.88 ± 0.14
103.9	19.8	−0.1863	7.29 ± 0.14
83.9	19.9	−0.2023	7.84 ± 0.15
64.0	19.9	−0.2199	8.46 ± 0.16
44.0	19.7	−0.2444	9.46 ± 0.18
29.1	10.0	−0.1383	10.54 ± 0.27
19.2	9.8	−0.1487	11.46 ± 0.30
9.3	9.8	−0.1586	12.15 ± 0.31

Table V. (*Continued*)

<i>P</i> (MPa)	<i>Ap</i> (MPa)	<i>I</i> (V · s)	α_p (10^{-4} K^{-1})
402.6 K			
343.3	20.3	-0.1220	4.41 ± 0.10
323.3	19.9	-0.1280	4.69 ± 0.11
303.4	19.7	-0.1315	4.83 ± 0.11
283.6	19.8	-0.1350	4.94 ± 0.11
263.7	19.8	-0.1391	5.09 ± 0.12
244.0	19.6	-0.1456	5.31 ± 0.12
224.1	19.9	-0.1522	5.47 ± 0.12
204.2	19.8	-0.1592	5.71 ± 0.13
184.2	19.9	-0.1665	5.94 ± 0.13
164.3	19.8	-0.1746	6.22 ± 0.14
143.3	20.0	-0.1843	6.49 ± 0.14
124.3	19.9	-0.1971	6.94 ± 0.15
104.4	19.9	-0.2111	7.40 ± 0.16
83.4	19.9	-0.2290	7.97 ± 0.17
64.5	19.8	-0.2537	8.80 ± 0.19
44.6	19.8	-0.2894	10.01 ± 0.21
29.7	9.9	-0.1679	11.50 ± 0.32
19.6	10.0	-0.1851	12.48 ± 0.34
9.6	10.0	-0.2093	14.09 ± 0.38
452.8 K			
344.0	19.8	-0.1264	4.41 ± 0.11
324.0	20.0	-0.1291	4.46 ± 0.11
303.9	20.1	-0.1332	4.57 ± 0.12
283.8	20.0	-0.1357	4.66 ± 0.12
263.8	19.8	-0.1416	4.88 ± 0.12
243.9	19.9	-0.1487	5.09 ± 0.13
223.9	19.9	-0.1546	5.26 ± 0.13
203.9	20.0	-0.1648	5.56 ± 0.14
183.9	19.9	-0.1747	5.88 ± 0.14
163.9	19.8	-0.1816	6.11 ± 0.15
144.0	19.9	-0.1930	6.45 ± 0.16
124.1	19.8	-0.2065	6.89 ± 0.19
104.1	20.0	-0.2244	7.39 ± 0.18
84.1	19.9	-0.2477	8.12 ± 0.20
64.1	19.8	-0.2783	9.09 ± 0.22
44.1	20.1	-0.3306	10.57 ± 0.25
28.9	10.0	-0.1967	12.51 ± 0.38
18.9	9.9	-0.2242	14.33 ± 0.43
8.8	10.1	-0.2694	16.88 ± 0.50

Table V. (Continued)

<i>P</i> (MPa)	<i>Δp</i> (MPa)	<i>I</i> (V · s)	α_p (10^{-4} K^{-1})
503.1 K			
343.0	20.3	-0.1241	4.09 ± 0.12
322.7	20.1	-0.1258	4.18 ± 0.13
302.5	20.2	-0.1307	4.31 ± 0.13
282.3	20.1	-0.1333	4.40 ± 0.13
262.1	19.9	-0.1382	4.58 ± 0.14
242.1	19.9	0.1452	4.79 ± 0.14
222.2	19.9	-0.1511	4.96 ± 0.15
202.2	19.9	-0.1603	5.24 ± 0.16
182.2	19.9	-0.1692	5.50 ± 0.16
162.2	19.9	-0.1810	5.83 ± 0.17
142.2	19.8	-0.1936	6.22 ± 0.18
122.3	19.9	-0.2073	6.61 ± 0.19
102.3	19.9	-0.2281	7.24 ± 0.21
82.3	20.0	-0.2541	7.97 ± 0.23
62.3	19.8	-0.2871	9.01 ± 0.26
42.4	20.0	-0.3490	10.74 ± 0.31
27.2	10.2	-0.2167	13.03 ± 0.45
17.0	10.1	-0.2635	15.88 ± 0.55
6.9	10.1	-0.4092	24.29 ± 0.84

Table VI. Results of Pressure-Controlled Scanning Calorimetric Measurements for the Isobaric Thermal Expansivities, α_p , of {0.6036 1-Hexanol-0.3964 *n*-Hexane} Mixture

<i>P</i> (MPa)	<i>Δp</i> (MPa)	<i>I</i> (V · s)	α_p (10^{-4} K^{-1})
302.6 K			
344.3	19.5	-0.0996	4.79 ± 0.19
324.5	19.9	-0.1022	4.82 ± 0.19
304.7	19.6	-0.1043	4.97 ± 0.19
284.8	19.9	-0.1060	4.79 ± 0.19
264.9	19.8	-0.1072	5.06 ± 0.20
245.1	19.8	-0.1132	5.32 ± 0.20
225.2	19.8	-0.1198	5.58 ± 0.21
205.4	19.7	-0.1239	5.78 ± 0.22
185.5	19.9	-0.1288	5.95 ± 0.23
165.7	19.6	-0.1310	6.12 ± 0.24
146.0	19.6	-0.1377	6.39 ± 0.25
126.2	19.8	-0.1451	6.66 ± 0.26
106.3	19.8	-0.1537	7.02 ± 0.37

Table VI. (Continued)

P (MPa)	Δp (MPa)	I (V · s)	α_p (10^{-4} K^{-1})
86.5	19.7	-0.1622	7.40 ± 0.28
66.6	19.8	-0.1743	7.91 ± 0.30
46.8	19.9	-0.1894	8.51 ± 0.32
31.7	10.0	-0.1032	9.14 ± 0.41
21.4	10.4	-0.1146	9.72 ± 0.43
11.2	9.9	-0.1159	10.34 ± 0.46
352.6 K			
343.7	19.7	-0.1143	4.69 ± 0.10
323.7	20.1	-0.1193	4.79 ± 0.10
303.6	19.9	-0.1180	4.78 ± 0.10
283.6	19.9	-0.1212	4.91 ± 0.10
263.8	19.6	-0.1247	5.11 ± 0.11
244.0	19.8	-0.1315	5.31 ± 0.11
224.1	19.8	-0.1347	5.42 ± 0.11
204.2	19.7	-0.1405	5.65 ± 0.11
184.3	19.9	-0.1477	5.87 ± 0.12
164.4	19.9	-0.1525	6.04 ± 0.12
144.6	19.6	-0.1621	6.49 ± 0.13
125.0	19.6	-0.1710	6.81 ± 0.13
105.3	19.7	-0.1824	7.19 ± 0.14
85.5	19.7	-0.1956	7.66 ± 0.15
65.7	19.7	-0.2129	8.30 ± 0.16
45.9	19.8	-0.2342	9.03 ± 0.17
30.9	10.0	-0.1290	9.85 ± 0.25
20.8	10.1	-0.1412	10.60 ± 0.37
10.8	10.0	-0.1516	11.43 ± 0.29
402.6 K			
343.5	20.0	-0.1216	4.46 ± 0.10
323.4	20.0	-0.1259	4.59 ± 0.10
303.4	19.9	-0.1307	4.76 ± 0.11
283.4	19.9	-0.1348	4.91 ± 0.11
263.5	19.7	-0.1379	5.04 ± 0.11
243.7	19.8	-0.1451	5.27 ± 0.12
223.8	19.9	-0.1510	5.43 ± 0.12
204.0	19.4	-0.1577	5.78 ± 0.13
184.4	19.8	-0.1669	5.98 ± 0.13
164.6	19.6	-0.1737	6.26 ± 0.14
144.9	19.8	-0.1851	6.58 ± 0.14
125.1	19.6	-0.1939	6.93 ± 0.15
105.4	19.7	-0.2099	7.40 ± 0.16
85.5	19.8	-0.2271	7.95 ± 0.17
65.7	19.8	-0.2497	8.70 ± 0.18
45.8	19.9	-0.2814	9.69 ± 0.20

Table VI. (Continued)

<i>P</i> (MPa)	<i>Δp</i> (MPa)	<i>I</i> (V · s)	α_p (10^{-4} K^{-1})
30.8	10.0	-0.1603	10.87 ± 0.30
20.7	10.0	-0.1775	11.97 ± 0.33
10.7	10.0	-0.1962	13.19 ± 0.36
452.8 K			
343.5	20.3	-0.1219	4.19 ± 0.11
323.1	20.2	-0.1347	4.58 ± 0.12
302.9	20.1	-0.1385	4.73 ± 0.12
282.8	19.9	-0.1425	4.90 ± 0.12
262.9	19.8	-0.1408	4.86 ± 0.12
243.0	19.8	-0.1474	5.08 ± 0.13
223.1	19.9	-0.1621	5.50 ± 0.14
203.1	19.8	-0.1692	5.72 ± 0.14
183.2	19.8	-0.1728	5.85 ± 0.15
163.3	19.8	-0.1778	5.99 ± 0.15
143.5	19.8	-0.1916	6.43 ± 0.16
123.6	19.8	-0.2021	6.75 ± 0.17
103.7	19.8	-0.2207	7.35 ± 0.18
83.9	19.8	-0.2575	8.25 ± 0.20
63.9	20.1	-0.2783	8.99 ± 0.22
43.8	20.0	-0.3222	10.37 ± 0.25
28.6	10.2	-0.1985	12.44 ± 0.37
18.5	9.9	-0.2176	13.92 ± 0.42
8.4	10.1	-0.2723	17.06 ± 0.51
503.1 K			
342.9	20.3	-0.1257	4.14 ± 0.13
322.5	20.3	-0.1246	4.10 ± 0.12
302.2	20.0	-0.1332	4.41 ± 0.13
282.0	20.1	-0.1409	4.63 ± 0.14
261.7	20.3	-0.1429	4.64 ± 0.14
241.5	20.0	0.1490	4.88 ± 0.15
221.6	19.8	-0.1513	4.98 ± 0.15
201.6	19.9	-0.1616	5.28 ± 0.16
181.7	19.9	-0.1765	5.71 ± 0.17
161.7	19.8	-0.1822	5.90 ± 0.17
141.8	19.9	-0.1932	6.21 ± 0.18
121.9	19.8	-0.2098	6.72 ± 0.20
102.0	19.8	-0.2341	7.45 ± 0.22
82.1	19.8	-0.2577	8.15 ± 0.24
62.3	19.8	-0.2949	9.23 ± 0.26
42.4	19.8	-0.3518	10.94 ± 0.31
27.4	10.1	-0.2171	13.14 ± 0.46
17.3	10.0	-0.2561	15.48 ± 0.54
7.2	10.1	-0.3746	22.29 ± 0.77

Table VII. Results of Pressure-Controlled Scanning Calorimetric Measurements for the Isobaric Thermal Expansivities, α_p , of {0.7455 1-Hexanol–0.2545 *n*-Hexane} Mixture

<i>P</i> (MPa)	<i>Δp</i> (MPa)	<i>I</i> (V · s)	α_p (10^{-4} K $^{-1}$)
302.6 K			
344.7	20.0	−0.0963	4.56 ± 0.18
324.6	20.0	−0.0979	4.62 ± 0.18
304.6	19.8	−0.0992	4.71 ± 0.18
284.7	19.8	−0.1023	4.85 ± 0.19
264.9	19.4	−0.1044	5.04 ± 0.20
245.4	19.6	−0.1097	5.21 ± 0.20
225.6	19.8	−0.1161	5.43 ± 0.21
205.7	19.8	−0.1206	5.61 ± 0.22
185.6	20.0	−0.1251	5.76 ± 0.22
165.6	19.8	−0.1270	5.88 ± 0.23
145.8	19.8	−0.1301	6.03 ± 0.23
125.9	19.7	−0.1384	6.41 ± 0.25
106.0	20.0	−0.1488	6.77 ± 0.26
85.9	20.0	−0.1577	7.12 ± 0.27
65.8	19.9	−0.1694	7.64 ± 0.29
45.8	20.0	−0.1823	8.20 ± 0.31
30.6	10.2	−0.0978	8.59 ± 0.38
20.6	9.8	−0.1038	9.40 ± 0.42
10.6	9.9	−0.1096	9.77 ± 0.44
352.6 K			
343.6	20.0	−0.1130	4.59 ± 0.10
323.6	20.0	−0.1138	4.62 ± 0.10
303.5	19.8	−0.1156	4.72 ± 0.10
283.6	19.9	−0.1191	4.83 ± 0.10
263.7	19.7	−0.1216	4.97 ± 0.10
243.9	19.8	−0.1262	5.12 ± 0.11
224.0	19.9	−0.1321	5.30 ± 0.11
204.0	19.8	−0.1373	5.51 ± 0.11
187.1	19.8	−0.1440	5.77 ± 0.12
164.4	19.6	−0.1502	6.04 ± 0.12
144.6	19.7	−0.1591	6.35 ± 0.13
124.8	19.8	−0.1682	6.64 ± 0.13
104.9	20.0	−0.1807	7.03 ± 0.14
84.8	20.1	−0.1924	7.42 ± 0.15
64.8	19.8	−0.2039	7.95 ± 0.16

Table VII. (Continued)

<i>P</i> (MPa)	<i>Ap</i> (MPa)	<i>I</i> (V · s)	α_p (10^{-4} K^{-1})
44.9	19.9	-0.2252	8.69 ± 0.17
29.9	10.1	-0.1257	9.54 ± 0.25
19.7	10.0	-0.1363	10.31 ± 0.26
9.6	10.1	-0.1482	11.14 ± 0.28
402.6 K			
344.6	20.0	-0.1243	4.53 ± 0.10
324.5	20.0	-0.1272	4.63 ± 0.11
304.5	19.8	-0.1295	4.75 ± 0.11
284.6	19.6	-0.1330	4.90 ± 0.11
264.8	19.8	-0.1354	4.94 ± 0.11
244.8	20.0	-0.1407	5.07 ± 0.11
224.8	19.9	-0.1483	5.34 ± 0.12
205.0	19.6	-0.1578	5.73 ± 0.13
185.1	20.0	-0.1601	5.70 ± 0.13
165.0	19.9	-0.1698	6.03 ± 0.13
145.1	19.6	-0.1814	6.50 ± 0.14
125.4	19.7	-0.1882	6.71 ± 0.15
105.4	20.1	-0.2040	7.09 ± 0.15
85.2	20.2	-0.2250	7.72 ± 0.17
65.0	19.9	-0.2437	8.44 ± 0.18
45.0	20.0	-0.2761	9.45 ± 0.20
29.9	10.0	-0.1562	10.60 ± 0.29
19.7	10.0	-0.1708	11.53 ± 0.32
9.7	9.9	-0.1890	12.83 ± 0.35
452.8 K			
344.4	20.3	-0.1249	4.27 ± 0.11
324.0	20.2	-0.1262	4.33 ± 0.11
303.9	19.7	-0.1320	4.60 ± 0.12
284.0	19.8	-0.1350	4.69 ± 0.12
264.1	19.9	-0.1454	4.97 ± 0.13
244.1	19.9	-0.1517	5.18 ± 0.13
224.1	19.9	-0.1599	5.42 ± 0.14
204.3	19.5	-0.1641	5.65 ± 0.14
184.4	19.9	-0.1708	5.76 ± 0.14
164.4	20.1	-0.1810	6.02 ± 0.15
144.3	20.0	-0.1944	6.45 ± 0.16

Table VII. (Continued)

P (MPa)	Δp (MPa)	I (V · s)	α_p (10^{-4} K^{-1})
124.3	19.7	-0.2080	6.98 ± 0.17
104.6	19.7	-0.2227	7.41 ± 0.18
84.6	20.0	-0.2424	7.92 ± 0.19
64.5	19.9	-0.2680	8.73 ± 0.21
44.5	20.0	-0.3148	10.15 ± 0.24
29.2	10.3	-0.1830	11.34 ± 0.34
18.9	10.9	-0.2139	13.48 ± 0.40
8.9	10.0	-0.2471	15.70 ± 0.47
503.1 K			
341.4	21.1	-0.1310	4.15 ± 0.12
320.3	20.9	-0.1353	4.31 ± 0.13
299.5	20.3	-0.1376	4.44 ± 0.13
278.9	20.3	-0.1405	4.57 ± 0.14
258.6	20.1	-0.1456	4.75 ± 0.14
238.4	20.1	-0.1527	4.99 ± 0.15
218.3	19.9	-0.1605	5.23 ± 0.16
198.1	20.0	-0.1722	5.57 ± 0.16
178.0	20.1	-0.1814	5.79 ± 0.17
157.8	20.1	-0.1845	5.91 ± 0.17
137.7	20.0	-0.1930	6.17 ± 0.18
117.1	19.9	-0.2139	6.81 ± 0.20
97.6	19.8	-0.2359	7.49 ± 0.22
77.6	20.0	-0.2639	8.23 ± 0.24
57.5	20.0	-0.2993	9.30 ± 0.27
42.2	10.1	-0.1723	10.49 ± 0.37
32.2	10.1	-0.1961	11.85 ± 0.41
22.0	10.0	-0.2316	14.03 ± 0.49
11.9	10.1	-0.2885	17.20 ± 0.59

Values of the coefficients are given in Table VIII. In Table VIII the standard and the average deviations between the experimental and the calculated values are also given. The major deviations between the experimental and calculated values are in the low-pressure range (up to about 15 MPa), where the relative errors of the present technique are the most important, due mainly to the uncertainties in the pressure measurements. However, despite the latter uncertainties, the standard deviations given in Table VIII are much smaller than the estimated maximal errors given in Tables I-VII.

Table VIII. Values of Coefficients in Eqs. (2)–(4) for the Particular Mixtures of *n*-Hexane with 1-Hexanol

Mixture, $X_{\text{1-hexanol}}$	a_0 ($10^{-2} \text{ K}^{-1} \text{ MPa}^{0.5}$)	a_1 ($10^{-5} \text{ K}^{-2} \text{ MPa}^{0.5}$)	a_2 ($10^{-8} \text{ K}^{-3} \text{ MPa}^{0.5}$)	b_0 (MPa)	b_1 ($\text{K}^{-1} \text{ MPa}$)	b_2 ($10^{-2} \text{ K}^{-2} \text{ MPa}$)	b_3 ($10^{-5} \text{ K}^{-3} \text{ MPa}$)	AVG ^a (%)	SD ^a (%)
0.0553	2.23023	-5.50363	4.85911	1131.70	-7.39381	1.65241	-1.25359	0.04	1.85
0.1088	2.08115	-4.70614	3.90970	1113.54	-7.09671	1.54602	-1.14491	0.06	1.83
0.2737	1.69215	-2.82831	1.83787	1012.23	-6.26019	1.33784	-0.979656	-0.04	1.59
0.2983	1.50043	-1.96649	0.884023	720.926	-4.19753	0.855969	-0.608101	0.03	1.22
0.4962	1.72864	-3.07480	2.24810	1226.05	-7.40577	1.53681	-1.03860	0.06	2.16
0.6036	1.66811	-2.88961	2.1897	1239.80	-7.45418	1.54739	-1.10000	0.05	2.19
0.7455	1.31597	-1.42609	0.716532	687.793	-3.48166	0.612619	-0.374463	0.05	1.72

^a AVG and SD are the average and standard deviations respectively, between the experimental and the calculated values.

4. DISCUSSION

The general behavior of $\alpha_p(p, T)$ for $\{n\text{-hexane} + 1\text{-hexanol}\}$ mixtures is similar to the behavior of $\alpha_p(p, T)$ for self-associated liquids, as in the case of *m*-cresol [12], where as the temperature increases, the isotherms cross at decreasing pressures. In the present case at high temperatures the pressure shift of the isotherm crossing becomes smaller and a unique crossing point appears, as for simple liquids. For a more detailed discussion, a set of low-temperature isotherms of α_p for selected mixtures of *n*-hexane with 1-hexanol is shown in Fig. 2, and a set of high-temperature isotherms in Fig. 3. In the two figures the single crossing point of α_p isotherms for pure *n*-hexane is also given; as a matter of fact, this point can be taken as a reference property (see Fig. 2a) to compare with the behavior of the mixtures. At lower temperatures the addition of 1-hexanol to *n*-hexane causes the isotherms to cross at higher pressures. At temperatures around 303 K the crossing of the isotherms is pushed from 70 MPa for pure *n*-hexane to about 200 MPa for $\{0.49621\text{-hexanol}-0.5038\text{-}n\text{-hexane}\}$ and to near 350 MPa for pure 1-hexanol. As the temperature increases the pressure at which the isotherms cross is shifted to lower values for all mixtures reported in the present study. In Fig. 2 one may notice that for all mixtures the isotherms at 403 K and 353 K cross at lower pressures

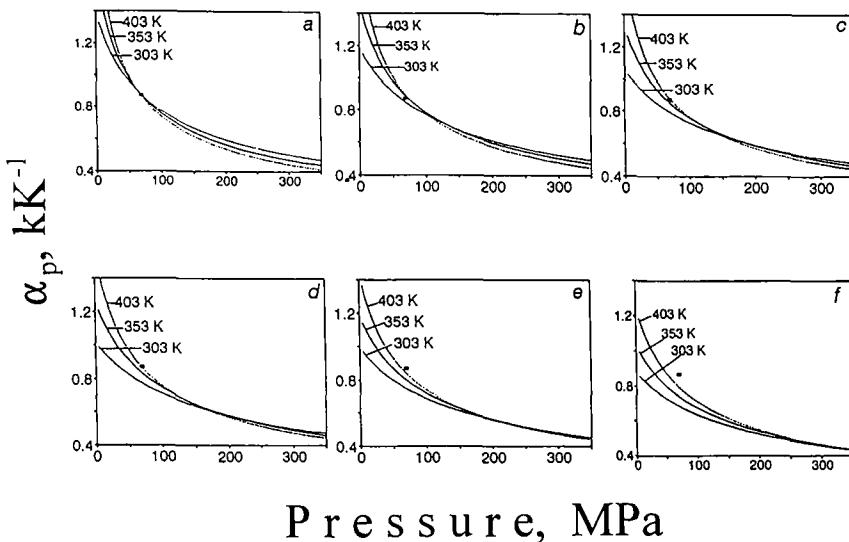


Fig. 2. Selected low-temperature isotherms of α_p for (a) *n*-hexane [8]; (b) a $\{0.27263\text{-}n\text{-hexane}\}$ mixture; (c) a $\{0.49621\text{-}1\text{-hexanol}-0.5038\text{-}n\text{-hexane}\}$ mixture; (d) a $\{0.60361\text{-}1\text{-hexanol}-0.3964\text{-}n\text{-hexane}\}$ mixture; (e) a $\{0.74551\text{-}1\text{-hexanol}-0.2545\text{-}n\text{-hexane}\}$ mixture; and (f) 1-hexanol [9]. (■) Crossing point of α_p isotherms for pure *n*-hexane.

than the isotherms at 353 and 303 K. A more detailed presentation of selected high-temperature isotherms is given in Fig. 3. At high temperatures the behavior of all mixtures studied is very similar to the behavior of *n*-hexane [8]: there are almost single crossing points and the coordinates of these points are close to those for *n*-hexane. Most likely at higher temperatures the association equilibrium is shifted to the monomer species and mixtures behave like the simple liquid, *n*-hexane. Probably, this situation will be even much more marked at temperatures higher than those reported in the present study. Over the temperature range of the present results there are also some singular observations to be made: at low concentrations of 1-hexanol the crossing point of isotherms is a bit shifted to lower pressures with respect to the crossing point of *n*-hexane and the value of α_p at the crossing point is higher than that for *n*-hexane. Most probably, this is related to the minimum of the negative branch of the excess volume in this system [7]. For mixtures with concentrations of 1-hexanol higher than 0.5 mol fraction, the crossing of isotherms is slightly shifted to higher pressures.

The overall behavior discussed above cannot be derived from known equations of state. Some encouraging results can be obtained when an

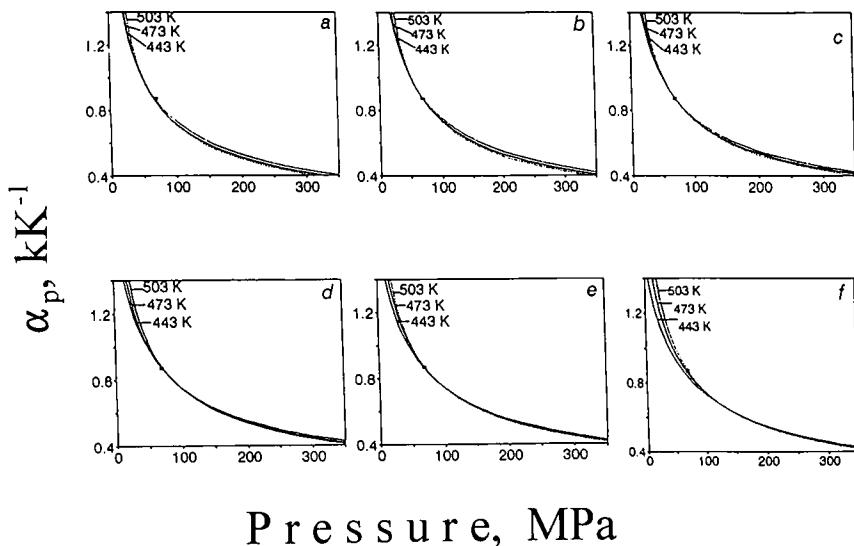


Fig. 3. Selected high-temperature isotherms of α_p for (a) a {0.1088 1-hexanol-0.8912 *n*-hexane} mixture; (b) a {0.2737 1-hexanol-0.7263 *n*-hexane} mixture; (c) a {0.4962 1-hexanol-0.5038 *n*-hexane} mixture; (d) a {0.6036 1-hexanol-0.3964 *n*-hexane} mixture; (e) a {0.7455 1-hexanol-0.2545 *n*-hexane} mixture; and (f) 1-hexanol [9]. (■) Crossing point of α_p isotherms for pure *n*-hexane.

additional term accounting for the association [13] is added to the soft-sphere equation of state [5]. The study is still in progress and detailed results as well as the analysis of this problem will be reported in subsequent studies.

5. CONCLUSIONS

The isobaric thermal expansivities for seven mixtures of *n*-hexane with 1-hexanol have been measured with a pressure-controlled scanning calorimeter over the temperature range from 303 to 503 K at pressures up to 350 MPa, which extends significantly the literature pressure-temperature surface for systems containing *n*-alkanes and *n*-alkanols. A detailed analysis of the present results reveals how the association equilibrium is affected by both pressure and temperature. At low temperatures the association equilibrium is the dominating factor in the thermodynamic behavior of the mixtures studied. At high temperatures the association phenomenon becomes weaker and the thermodynamic behavior of the mixtures approaches the well known behavior of *n*-hexane. The present data should contribute to an IUPAC project [7] to establish recommended data sets for the thermodynamic properties of pure alkanols, alkanes, and their mixtures. The present contribution is especially concerned with the effect of pressure and temperature on those properties. As the isobaric coefficient of thermal expansion is easily derived from an equation of state, the present data should also serve as an experimental base for further developments of equations of state for associated fluids valid over wide ranges of pressure and temperature.

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REFERENCES

1. S. L. Randzio, D. J. Eatough, E. A. Lewis, and L. D. Hansen, *J. Chem Thermodyn.* **20**:37 (1988).
2. S. L. Randzio, J.-P. E. Grolier, and J. R. Quint, *Rev. Sci. Instrum.* **65**:960 (1994).
3. S. L. Randzio, *Phys. Lett. A* **117**:473 (1986).
4. S. L. Randzio and U. K. Deiters, *Ber. Bunsenges. Phys. Chem.* **99**:1179 (1995).
5. U. K. Deiters and S. L. Randzio, *Fluid Phase Equil.* **103**:199 (1995).
6. S. L. Randzio, J.-P. E. Grolier, and J. R. Quint, *J. Therm. Anal.* **38**:1960 (1992).

7. A. H. Roux, G. Roux-Degranges, and J.-P. E. Grolier, *Fluid Phase Equil.* **89**:57 (1993).
8. S. L. Randzio, J.-P. E. Grolier, J. R. Quint, D. J. Eatough, E. A. Lewis, and L. D. Hansen, *Int. J. Thermophys.* **15**:415 (1994).
9. S. L. Randzio, J.-P. E. Grolier, and J. R. Quint, *Fluid Phase Equil.* **110**:341 (1995).
10. Ph. Pruzan, *J. Chem. Thermodyn.* **23**:247 (1991).
11. S. L. Randzio, *Chem. Soc. Rev.* **24**:359 (1995).
12. S. L. Randzio, E. A. Lewis, D. J. Eatough, and L. D. Hansen, *Int. J. Thermophys.* **16**:883 (1995).
13. U. K. Deiters, *Fluid Phase Equil.* **89**:229 (1993).