International Journal of Thermophysics, Vol. 18, No. 5, 1997

Isobaric Thermal Expansivities of Mixtures of *m*-Cresol and Quinoline from 0.1 to 400 MPa at 303 to 503 K

S. L. Randzio,[1,2] L. D. Hansen,[3] E. A. Lewis,[3] and D. J. Eatough[3]

Received November 8, 1996

Isobaric thermal expansivities, $\alpha_p(p, T)$, of five binary mixtures of *m*-cresol with quinoline (0.1499, 0.2998, 0.5005, 0.6325, and 0.8501 mol fraction of *m*-cresol) were measured in a pressure-controlled scanning calorimeter over the pressure range from just above the saturation vapor pressures to 400 MPa, and at 303.15, 353.15, 403.15, 453.15, and 503.15 K. Molecular association of *m*-cresol with itself and of *m*-cresol with quinoline exerts large effects on the pressure and temperature behavior of α_p isotherms. The extent of association changes significantly with conditions in all except the 2:1 mixture as demonstrated by the crossing of isotherms at lower pressures as the temperature increases. In the 2:1 *m*-cresol quinoline mixture the extent of association is not perturbed significantly by temperature change and the mixture behaves like a simple liquid, exhibiting a unique crossing point of α_p isotherms.

KEY WORDS: binary mixtures; *m*-cresol; pressure-controlled scanning calorimetry; quinoline; thermal expansivity.

1. INTRODUCTION

m-Cresol, quinoline, and their mixtures are of practical importance as models for understanding the behavior of the components of heavy petroleum, shale oil, tar sands, and synthetic coal-liquids. Developing new means for upgrading these alternate fuels requires accurate data on the thermophysical properties of the components over wide ranges of pressure

---

[1] Institute of Physical Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, Pl-01-224 Warszawa, Poland.

[2] To whom correspondence should be addressed.

[3] Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84602, U.S.A.

and temperature. Most such thermodynamic data have been collected as a function of temperature under saturation pressure or under slightly elevated pressure. Accurate data on the pressure derivatives of the thermodynamic functions are not available except for those we recently reported for *m*-cresol [1] and quinoline [2] over the temperature range from 303 to 503 K at pressures up to 400 MPa. The present study reports results of pressure-scanning calorimetric measurements of α_p for binary mixtures of *m*-cresol with quinoline at five concentrations, at pressures up to 400 MPa, and at temperatures of 303.15, 353.15, 403.15, 453.15, and 503.15 K.

Previous studies [3] have established that the isotherms of the isobaric coefficient of thermal expansion, α_p, for simple liquids without specific interactions exhibit a unique crossing point where α_p is independent of temperature. The pressure–temperature behavior of α_p for associated liquids is much more complex and depends on the nature of the specific interactions. Understanding these phenomena requires experimental investigation of various associated liquids over wide ranges of pressure and temperature. Such data are available [4–6] for mixtures of 1-hexanol and *n*-hexane in which only 1-hexanol is self-associated and no specific interactions occur between the two components. Mixtures of *m*-cresol and quinoline are examples of liquid mixtures with strong specific interactions, specifically 1:1 and 2:1 complexes, between the components [7, 8]. In the pure state, *m*-cresol is a strongly self-associated liquid [9], but quinoline is only weakly self-associated [7]. The excess enthalpy–concentration curve for *m*-cresol–quinoline mixtures is not symmetric and has a maximum of $-7.7\ \mathrm{kJ\ mol^{-1}}$ near 0.6 mol fraction of *m*-cresol [8].

2. EXPERIMENTAL PROCEDURE

Measurements of thermal expansivities were performed in a pressure-controlled scanning calorimeter described previously [10]. Calorimetric determination of the isobaric coefficient of thermal expansion is based on the Maxwell relation, which states that the isothermal pressure derivative of entropy is equal to, but of opposite sign to, the isobaric temperature derivative of volume. When pressure is scanned as a stepwise function of time at a constant temperature, the mean value of the isobaric coefficient of thermal expansion, $\langle \alpha_{p,n} \rangle$, over the pressure step Δp_n, is calculated from the pressure change and heat effect as shown in Eq. (1).

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

where I_n (V·s) is the time integral of the calorimetric signal (heat rate) resulting from the calorimeter response to the pressure step Δp_n (MPa) performed under quasi-isothermal conditions, $\alpha_{p,\mathrm{SS}}$ ($5.1 \times 10^{-5}\ \mathrm{K}^{-1}$) is the thermal expansivity of the stainless steel of the calorimetric vessel, T is the absolute temperature, and k($\mathrm{MPa} \cdot \mathrm{V}^{-1} \cdot \mathrm{s}^{-1}$) is the temperature-dependent calibration constant. Details of the calibration procedures and on verification of this method are given in previous publications [3, 10, 11].

The *m*-cresol used in this study was Aldrich Gold Label No. C8572, 99+% and quinoline was Aldrich No. 25,401.0, 99+%, both used without further purification. Mixtures were prepared by weight. To prevent sorption of moisture, the mixtures were transferred into the calorimetric vessel with a syringe immediately after preparation. The calorimetric vessel 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, always near 400 MPa, 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.

3. RESULTS

Isobaric thermal expansivities measured at 303.15, 353.15, 403.15, 453.15, and 503.15 K as a function of pressure are given in Tables I–V for the five binary mixtures investigated. The pressures given in Tables I–V are the means of the beginning and ending pressures of the pressure steps. The end values were measured at the end of the thermogram 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 combining the uncertainties in the measured pressures (±0.14 MPa), the integrals I (±0.2%), the temperatures (±0.1 K), $\alpha_{p,\mathrm{SS}}$ (±5%), and the calibration constant k (from ±0.4% to ±1.7% depending on the temperature as reported in Ref. 10).

The experimental results for the liquid phase were fitted by least squares to a correlation equation [Eq. (2)].

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

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

$$a(T) = a_0 + a_1 T + a_2 T^2 \tag{3}$$

and

$$b(T) = b_0 + b_1 T + b_2 T^2 \tag{4}$$

Table I. Isobaric Thermal Expansivities, α_p, of a {0.1499 *m*-Cresol + 0.8501 Quinoline} Mixture

P (MPa)	Δp (MPa)	$-I^a$ (V·s)	α_p (10^{-4} K^{-1})	p (MPa)	Δp (MPa)	$-I^a$ (V·s)	α_p (10^{-4} K^{-1})
303.15 K							
15.8	25.6	0.2105	7.02 ± 0.19	207.2	26.9	0.1508	4.95 ± 0.13
69.7	27.7	0.1957	6.10 ± 0.16	239.8	28.3	0.1566	4.89 ± 0.13
97.7	28.3	0.1894	5.81 ± 0.15	262.6	27.3	0.2079	6.53 ± 0.17
124.6	25.6	0.1667	5.66 ± 0.15	292.8	25.8	0.9354	29.20 ± 0.73
151.1	27.3	0.1710	5.46 ± 0.15	319.2	27.1	0.6097	18.17 ± 0.45
179.2	29.0	0.1657	5.02 ± 0.13	346.3	27.2	0.4076	12.38 ± 0.31
353.15 K							
10.0	17.2	0.1626	7.57 ± 0.13	186.8	28.1	0.1693	5.00 ± 0.08
30.6	24.1	0.2143	7.15 ± 0.10	215.2	28.7	0.1625	7.73 ± 0.07
55.5	25.6	0.2116	6.67 ± 0.10	242.8	26.6	0.1524	4.78 ± 0.07
80.1	23.7	0.1817	6.22 ± 0.09	269.8	27.4	0.1503	4.60 ± 0.07
104.9	25.9	0.1867	5.89 ± 0.09	296.9	26.8	0.1396	4.40 ± 0.07
132.3	27.0	0.1825	5.84 ± 0.08	324.1	27.6	0.1406	4.31 ± 0.07
159.3	26.9	0.1748	5.35 ± 0.08	351.8	27.9	0.1314	3.96 ± 0.06
403.15 K							
7.45	13.5	0.1426	7.95 ± 0.15	187.2	27.4	0.1754	5.02 ± 0.07
27.1	25.8	0.2485	7.30 ± 0.10	214.7	27.7	0.1705	4.84 ± 0.07
51.7	23.4	0.2077	6.75 ± 0.10	242.0	26.9	0.1547	4.56 ± 0.07
77.2	27.4	0.2143	6.01 ± 0.09	269.3	27.8	0.1533	4.37 ± 0.07
104.3	26.1	0.2019	5.96 ± 0.09	298.0	27.6	0.1454	4.22 ± 0.07
131.9	28.4	0.2038	5.56 ± 0.08	325.7	27.6	0.1406	4.10 ± 0.06
159.8	27.4	0.1860	5.30 ± 0.08	353.5	28.0	0.1196	3.52 ± 0.06
453.15 K							
10.4	17.9	0.2102	8.53 ± 0.18	179.6	28.8	0.1894	5.00 ± 0.10
30.0	21.2	0.2174	7.51 ± 0.16	237.0	27.4	0.1581	4.44 ± 0.09
63.1	45.0	0.4082	6.68 ± 0.12	264.4	27.5	0.1566	4.39 ± 0.09
99.0	26.8	0.2217	6.14 ± 0.12	293.8	31.1	0.1723	4.28 ± 0.09
125.3	25.9	0.2081	5.99 ± 0.12	323.4	28.3	0.1570	4.29 ± 0.09
151.7	27.0	0.1943	5.42 ± 0.11	351.5	27.9	0.1371	3.86 ± 0.08
503.15 K							
11.4	18.7	0.2434	9.00 ± 0.24	180.0	27.6	0.1706	4.54 ± 0.12
30.7	19.9	0.2079	7.31 ± 0.19	207.2	26.9	0.1664	4.54 ± 0.12
52.2	23.0	0.2285	6.98 ± 0.18	234.9	28.5	0.1693	4.38 ± 0.11
75.9	24.4	0.2124	6.18 ± 0.16	263.1	27.9	0.1494	4.00 ± 0.10
100.0	23.6	0.1839	5.59 ± 0.14	292.4	30.8	0.1598	3.89 ± 0.10
124.8	25.9	0.1916	5.34 ± 0.14	351.4	31.2	0.1456	3.55 ± 0.09
151.9	28.5	0.1998	5.08 ± 0.13				

[a] I is the integral of the calorimetric response to the quasi-isothermal pressure variation Δp.

Table II. Isobaric Thermal Expansivities, α_p, of a $\{0.2998$ *m*-Cresol $+ 0.7002$ Quinoline$\}$ Mixture

P (MPa)	Δp (MPa)	$-I$ (V·s)	α_p (10^{-4} K^{-1})	p (MPa)	Δp (MPa)	$-I$ (V·s)	α_p (10^{-4} K^{-1})
303.15 K							
31.6	22.1	0.1772	6.84 ± 0.19	214.7	26.7	0.1523	5.03 ± 0.14
54.9	24.3	0.1820	6.43 ± 0.17	241.4	26.8	0.1451	4.79 ± 0.13
79.5	25.0	0.1755	6.06 ± 0.16	269.6	29.4	0.1481	4.49 ± 0.12
105.1	26.1	0.1691	5.64 ± 0.15	300.2	31.9	0.1483	4.19 ± 0.11
131.7	27.2	0.1729	5.54 ± 0.15	329.9	27.6	0.1310	4.27 ± 0.12
158.4	26.3	0.1593	5.29 ± 0.14	357.1	26.8	0.1292	4.17 ± 0.11
185.6	28.1	0.1636	5.12 ± 0.14				
353.15 K							
11.0	19.6	0.1958	7.96 ± 0.12	203.7	19.8	0.1501	5.98 ± 0.12
31.1	20.6	0.1797	7.02 ± 0.11	210.7	27.4	0.1561	4.76 ± 0.07
52.7	22.8	0.1817	6.46 ± 0.10	238.1	27.5	0.1553	4.71 ± 0.07
76.0	23.8	0.1833	6.25 ± 0.09	265.6	27.4	0.1448	4.45 ± 0.07
101.0	26.2	0.1874	5.84 ± 0.09	293.0	27.5	0.1400	4.30 ± 0.07
127.4	26.5	0.1857	5.72 ± 0.09	320.6	27.7	0.1420	4.34 ± 0.07
155.3	29.2	0.1852	5.23 ± 0.08	355.1	23.0	0.0977	3.67 ± 0.06
183.4	27.1	0.1692	5.16 ± 0.08				
403.15 K							
16.1	23.7	0.2508	7.99 ± 0.11	200.7	26.3	0.1661	4.97 ± 0.08
67.9	26.6	0.2259	6.49 ± 0.09	233.5	39.2	0.2359	4.75 ± 0.07
94.1	25.8	0.2029	6.06 ± 0.09	266.8	27.6	0.1525	4.41 ± 0.07
119.9	25.7	0.1894	5.70 ± 0.08	296.3	25.6	0.1367	4.28 ± 0.07
146.2	26.9	0.1869	5.40 ± 0.08	323.5	28.8	0.1438	4.03 ± 0.06
173.6	28.0	0.1823	5.10 ± 0.08	352.4	29.0	0.1379	3.86 ± 0.06
453.15 K							
11.3	13.4	0.1778	9.24 ± 0.22	173.0	26.3	0.1715	4.94 ± 0.10
28.7	20.9	0.2231	7.78 ± 0.16	225.0	26.8	0.1647	4.70 ± 0.10
50.0	20.7	0.2017	7.15 ± 0.15	250.6	24.3	0.1375	4.37 ± 0.09
71.4	22.1	0.1921	6.44 ± 0.13	276.0	26.5	0.1407	4.12 ± 0.09
95.3	25.8	0.2081	6.00 ± 0.12	307.4	36.4	0.1874	4.01 ± 0.08
121.1	25.9	0.2014	5.80 ± 0.12	339.4	27.6	0.1354	3.85 ± 0.08
147.0	25.7	0.1801	5.28 ± 0.11				
503.15 K							
11.6	19.8	0.2595	9.06 ± 0.24	206.5	26.9	0.1487	4.11 ± 0.11
34.4	25.7	0.2595	7.09 ± 0.18	233.2	26.4	0.1549	4.33 ± 0.11
60.5	26.5	0.2594	6.88 ± 0.17	259.2	25.7	0.1513	4.35 ± 0.11
86.6	25.7	0.2273	6.28 ± 0.16	287.0	26.5	0.1488	4.16 ± 0.11
112.5	26.2	0.2108	5.75 ± 0.15	314.4	28.3	0.1610	4.22 ± 0.11
145.9	40.5	0.2938	5.24 ± 0.12	342.6	28.1	0.1261	3.43 ± 0.09
179.6	27.0	0.1649	4.50 ± 0.12				

Table III. Isobaric Thermal Expansivities, α_p, of a {0.5005 *m*-Cresol + 0.4995 Quinoline} Mixture

p (MPa)	Δp (MPa)	$-I$ (V·s)	α_p (10^{-4} K^{-1})	p (MPa)	Δp (MPa)	$-I$ (V·s)	α_p (10^{-4} K^{-1})
			303.15 K				
13.6	23.2	0.1938	7.13 ± 0.19	195.5	28.1	0.1657	5.17 ± 0.14
38.7	27.0	0.2118	6.71 ± 0.18	224.4	29.7	0.1660	4.94 ± 0.13
64.5	24.7	0.1813	6.32 ± 0.17	251.3	24.1	0.1296	4.77 ± 0.13
91.2	28.6	0.1971	5.95 ± 0.16	276.3	26.1	0.1401	4.77 ± 0.13
118.2	25.5	0.1697	5.77 ± 0.15	301.7	24.8	0.1267	4.55 ± 0.13
143.5	25.0	0.1592	5.55 ± 0.15	324.9	21.7	0.1039	4.29 ± 0.12
168.8	25.5	0.1521	5.24 ± 0.14				
			353.15 K				
10.6	19.7	0.1817	7.55 ± 0.12	186.9	26.8	0.1678	5.18 ± 0.08
31.0	22.1	0.1999	7.35 ± 0.11	214.0	29.1	0.1802	5.13 ± 0.08
54.2	24.5	0.2075	6.82 ± 0.10	242.2	27.2	0.1599	4.88 ± 0.08
80.3	26.3	0.2076	6.38 ± 0.09	272.5	33.4	0.1898	4.74 ± 0.07
106.2	25.4	0.1871	6.00 ± 0.09	302.9	27.5	0.1492	4.55 ± 0.07
132.0	26.3	0.1836	5.71 ± 0.09	327.3	29.2	0.1156	4.58 ± 0.07
158.9	27.6	0.1803	5.38 ± 0.08				
			403.15 K				
11.0	19.3	0.2107	8.21 ± 0.13	189.7	25.8	0.1721	5.41 ± 0.08
32.9	32.8	0.2430	7.53 ± 0.10	222.3	29.6	0.1843	4.89 ± 0.07
58.5	26.8	0.2441	6.92 ± 0.10	249.4	24.5	0.1467	4.72 ± 0.07
83.9	23.9	0.2046	6.54 ± 0.10	273.1	22.8	0.1334	4.63 ± 0.08
108.8	25.9	0.2117	6.28 ± 0.09	295.4	21.9	0.1262	4.58 ± 0.08
135.6	27.7	0.2076	5.79 ± 0.08	316.2	19.7	0.1088	4.41 ± 0.08
163.1	27.4	0.1969	5.57 ± 0.08				
			453.15 K				
10.5	17.7	0.2271	9.24 ± 0.20	182.0	27.7	0.1918	5.23 ± 0.11
28.7	18.8	0.2100	8.11 ± 0.17	209.7	27.7	0.1901	5.18 ± 0.11
53.4	24.1	0.2413	7.32 ± 0.15	236.9	26.8	0.1696	4.83 ± 0.10
76.5	22.1	0.2003	6.71 ± 0.14	264.2	27.9	0.1686	4.62 ± 0.10
100.3	25.4	0.2171	6.33 ± 0.13	292.9	29.3	0.1835	4.55 ± 0.09
127.5	29.0	0.2245	5.78 ± 0.11	318.0	20.9	0.1112	4.13 ± 0.09
155.1	26.2	0.1957	5.60 ± 0.11				
			503.15 K				
16.7	20.3	0.2705	9.18 ± 0.24	212.9	26.5	0.1766	4.84 ± 0.12
39.3	24.8	0.2742	7.73 ± 0.19	239.6	27.0	0.1696	4.61 ± 0.12
63.1	22.8	0.2319	7.13 ± 0.18	266.5	26.8	0.1597	4.39 ± 0.11
138.2	25.5	0.1993	5.60 ± 0.14	293.1	26.3	0.1575	4.40 ± 0.11
164.2	26.6	0.1950	5.28 ± 0.13	318.2	23.8	0.1313	4.11 ± 0.11
188.6	22.1	0.1517	4.99 ± 0.13				

Table IV. Isobaric Thermal Expansivities, α_p, of a {0.6325 *m*-Cresol + 0.3675 Quinoline} Mixture

P (MPa)	Δp (MPa)	$-I$ (V·s)	α_p (10^{-4} K^{-1})	p (MPa)	Δp (MPa)	$-I$ (V·s)	α_p (10^{-4} K^{-1})
			303.15 K				
10.2	18.2	0.1542	7.21 ± 0.21	210.2	27.3	0.1599	5.14 ± 0.14
30.0	21.4	0.1721	6.88 ± 0.19	239.5	31.3	0.1701	4.81 ± 0.13
51.8	23.8	0.1774	6.10 ± 0.17	268.6	26.9	0.1398	4.62 ± 0.13
76.2	25.5	0.1825	6.17 ± 0.16	295.8	27.6	0.1375	4.45 ± 0.13
102.0	26.1	0.1745	5.79 ± 0.15	323.0	26.9	0.1265	4.23 ± 0.12
128.8	27.4	0.1790	5.68 ± 0.15	349.2	25.4	0.1156	4.10 ± 0.11
156.0	27.2	0.1700	5.46 ± 0.15				
			353.15 K				
18.8	17.4	0.1700	7.80 ± 0.13	170.2	29.4	0.1901	5.32 ± 0.07
28.7	21.2	0.1959	7.38 ± 0.11	228.3	27.4	0.1483	4.55 ± 0.07
49.5	20.3	0.1799	7.10 ± 0.11	255.8	27.6	0.1523	4.62 ± 0.07
69.1	19.1	0.1575	6.66 ± 0.11	283.2	27.2	0.1366	4.22 ± 0.07
91.0	24.8	0.1959	6.39 ± 0.09	313.2	32.8	0.1711	4.40 ± 0.07
116.5	26.1	0.1937	6.05 ± 0.09	341.3	23.4	0.1174	4.25 ± 0.07
142.9	26.0	0.1794	5.65 ± 0.08				
			403.15 K				
11.6	18.3	0.1931	7.96 ± 0.13	157.6	27.1	0.1977	5.65 ± 0.08
31.0	20.7	0.2143	7.81 ± 0.12	184.4	26.6	0.1830	5.36 ± 0.08
52.7	22.8	0.2138	7.13 ± 0.10	238.5	27.1	0.1689	4.90 ± 0.07
77.2	26.2	0.2281	6.64 ± 0.09	293.4	26.9	0.1485	4.40 ± 0.07
103.6	26.5	0.2198	6.34 ± 0.09	349.1	32.1	0.1460	3.72 ± 0.06
130.5	27.2	0.2045	5.81 ± 0.08				
			453.15 K				
11.5	18.9	0.2210	8.48 ± 0.18	183.9	28.1	0.1945	5.23 ± 0.11
31.3	20.5	0.2253	8.00 ± 0.17	239.6	26.8	0.1676	4.77 ± 0.10
53.5	24.1	0.2440	7.42 ± 0.15	267.8	29.4	0.1627	4.27 ± 0.09
77.8	24.4	0.2266	6.83 ± 0.14	296.5	28.0	0.1566	4.32 ± 0.09
103.4	26.9	0.2259	6.23 ± 0.12	327.5	27.5	0.1406	3.99 ± 0.09
129.8	25.8	0.1997	5.78 ± 0.12	354.0	25.6	0.1149	3.57 ± 0.08
156.2	27.2	0.2079	5.72 ± 0.11				
			503.15 K				
11.6	19.7	0.2851	9.96 ± 0.26	213.0	25.6	0.1814	5.13 ± 0.13
32.9	23.0	0.2813	8.47 ± 0.21	239.7	27.9	0.1731	4.56 ± 0.12
57.5	26.3	0.2648	7.07 ± 0.18	266.8	26.3	0.1523	4.29 ± 0.11
82.7	24.1	0.2127	6.27 ± 0.16	293.1	26.3	0.1544	4.33 ± 0.11
132.3	26.3	0.2238	6.05 ± 0.15	319.3	26.3	0.1554	4.36 ± 0.11
158.7	26.3	0.1975	5.40 ± 0.14	348.3	31.6	0.1663	3.94 ± 0.10
185.4	27.2	0.1905	5.08 ± 0.13				

Table V. Isobaric Thermal Expansivities, α_p, of a {0.8501 *m*-Cresol + 0.1499 Quinoline} Mixture

P (MPa)	Δp (MPa)	$-I$ (V·s)	α_p (10^{-4} K^{-1})	p (MPa)	Δp (MPa)	$-I$ (V·s)	α_p (10^{-4} K^{-1})
303.15 K							
11.0	19.3	0.1674	7.37 ± 0.21	187.8	26.8	0.1554	5.09 ± 0.14
33.6	25.9	0.2105	6.95 ± 0.18	214.4	26.2	0.1515	5.09 ± 0.14
58.2	23.2	0.1790	6.60 ± 0.18	240.6	26.3	0.1443	4.86 ± 0.13
82.0	24.4	0.1779	6.28 ± 0.17	293.7	27.9	0.1478	4.71 ± 0.13
107.7	25.9	0.1709	5.74 ± 0.15	321.8	28.6	0.1432	4.47 ± 0.12
134.1	26.9	0.1654	5.68 ± 0.15	348.7	25.2	0.1207	4.29 ± 0.12
161.0	26.9	0.1757	2.38 ± 0.14				
353.15 K							
11.4	19.3	0.1951	8.04 ± 0.13	242.0	26.0	0.1540	4.92 ± 0.08
56.9	27.5	0.2389	6.98 ± 0.10	268.0	25.9	0.1485	4.79 ± 0.14
85.0	25.1	0.2021	6.51 ± 0.10	294.4	26.9	0.1453	4.54 ± 0.07
110.5	25.9	0.1941	5.02 ± 0.11	326.9	27.3	0.1409	4.36 ± 0.07
136.6	26.5	0.1870	5.76 ± 0.09	354.3	27.6	0.1356	4.17 ± 0.07
215.5	26.8	0.1689	5.20 ± 0.08				
403.15 K							
11.1	18.6	0.2167	8.71 ± 0.14	223.9	25.2	0.1615	5.03 ± 0.08
31.2	21.5	0.2328	8.14 ± 0.12	250.4	25.1	0.1580	4.95 ± 0.08
93.2	25.0	0.2037	6.26 ± 0.09	275.9	26.0	0.1567	4.76 ± 0.07
118.7	26.1	0.1962	5.81 ± 0.09	302.0	26.2	0.1512	4.58 ± 0.07
145.0	26.5	0.1829	5.36 ± 0.08	327.5	24.8	0.1328	3.77 ± 0.06
171.5	26.6	0.1770	5.20 ± 0.08	353.9	27.9	0.1234	3.62 ± 0.06
190.1	26.5	0.1803	4.95 ± 0.08				
453.15 K							
12.0	20.1	0.2599	9.30 ± 0.19	183.4	27.1	0.1845	5.15 ± 0.11
33.4	23.7	0.2609	8.00 ± 0.16	210.9	23.9	0.1565	4.98 ± 0.11
57.4	24.3	0.2521	7.58 ± 0.15	236.1	26.7	0.1676	4.79 ± 0.10
81.3	23.6	0.2148	6.71 ± 0.14	263.3	27.7	0.1650	4.56 ± 0.09
106.5	24.0	0.2021	6.26 ± 0.13	290.8	27.2	0.1613	4.55 ± 0.09
131.5	26.0	0.2084	5.97 ± 0.12	317.8	27.0	0.1551	4.43 ± 0.09
158.1	27.4	0.2055	5.62 ± 0.11	345.1	27.6	0.1569	4.38 ± 0.09
503.15 K							
10.5	16.9	0.2516	10.22 ± 0.28	214.4	25.4	0.1689	4.85 ± 0.13
27.1	16.3	0.2057	8.71 ± 0.24	239.7	25.7	0.1650	4.69 ± 0.12
71.1	26.0	0.2554	6.91 ± 0.17	265.7	25.8	0.1575	4.49 ± 0.12
98.1	27.9	0.2431	6.18 ± 0.15	296.8	28.4	0.1628	4.24 ± 0.11
125.7	27.2	0.2172	5.71 ± 0.14	325.6	29.3	0.1533	3.92 ± 0.10
153.0	27.4	0.2068	5.42 ± 0.14	353.6	26.6	0.1329	3.76 ± 0.10
184.2	35.0	0.2519	5.21 ± 0.13				

Table VI. Values of Coefficients in Eqs. (2)–(4) for Mixtures of *m*-Cresol with Quinoline[a]

Mixture ($X_{m\text{-cresol}}$)	a_0 (10^{-2} K^{-1}·MPa$^{0.5}$)	a_1 (10^{-5} K^{-2}·MPa$^{0.5}$)	a_2 (10^{-8} K^{-3}·MPa$^{0.5}$)	b_0 (MPa)	b_1 (K^{-1}·MPa)	b_2 (10^{-3} K^{-2}·MPa)	AVG (%)	STD (%)
0.1499	0.7089	1.64929	−3.19114	341.32	−0.702564	0.285322	0.10	3.08
0.2998	1.5252	−2.49190	1.83671	677.33	−2.42637	2.37982	0.04	3.57
0.5005	1.3514	−1.07543	−0.039699	694.51	−2.22260	1.92028	0.02	1.65
0.6325	1.4173	−2.04480	1.61292	544.48	−1.75425	1.56869	0.29	3.85
0.8501	1.55632	−2.49338	1.90909	636.34	−2.17852	2.02446	0.21	3.84

[a] The coefficients are valid for the liquid phase from 353 to 503 K at pressures up to 400 MPa. AVG and STD are the average and standard deviations between the experimental data and the values calculated from the equations.

Values of the coefficients are given in Table VI, which also gives both standard (STD) and average (AVG) deviations between experimental and calculated values. The major deviations between experimental and calculated values are in the low-pressure range (up to about 15 MPa), where the relative errors of the present technique are due mainly to the uncertainties in the pressure measurements. The fitted values are valid for the liquid phase over the temperature range from 353 to 503 K at pressures up to 400 MPa.

4. DISCUSSION

The behavior of $\alpha_p(p, T)$ for *m*-cresol, quinoline, and their mixtures depends on the nature of the intermolecular interactions in the liquids. Quinoline is a very weakly self-associated liquid [7] and thus its α_p isotherms exhibit a unique crossing point (see Fig. 1a) [2], similar to the behavior of *n*-hexane [4]. The α_p isotherms of *m*-cresol cross near 100 MPa, but the crossing points are temperature dependent, crossing at lower pressures as the temperature increases (see Fig. 1f) [1]. This behavior is a result of shifting of the cresol self-association equilibrium with p and T.

Mixtures of *m*-cresol and quinoline near a 2:1 mol ratio behave like liquids without specific association, i.e., the α_p isotherms exhibit a unique crossing point at $p = 170$ MPa and $\alpha_p = (5.27 \pm 0.01) \times 10^{-4}\ \mathrm{K}^{-1}$ over the temperature range from 353 to 503 K (see Fig. 1d). Mixtures with lower and higher concentrations of *m*-cresol behave similarly to *m*-cresol, i.e., the α_p isotherms cross at lower pressures as the temperature increases (see Figs. 1b and e). The behavior of the 2:1 mixture is explained by the very strong 2:1 association between *m*-cresol and quinoline. The position of this equilibrium is not much disturbed by changes in pressure and temperature over the ranges of pressure and temperature used in this study. Recall also that near the 2:1 mol ratio, the excess enthalpy of mixing is at a maximum near $-7.7\ \mathrm{kJ\,mol}^{-1}$ [8]. In the 2:1 mixture, the liquid phase is composed of strongly bound intermolecular complexes which behave like the molecules of a liquid without specific association. Thus, the macroscopic properties of such a phase are similar to those of nonpolar liquids. In mixtures with other than a 2:1 mol ratio of *m*-cresol to quinoline the equilibria among the 2:1 and 1:1 complexes between *m*-cresol and quinoline [7] and self-associated polymers of *m*-cresol, i.e., dimers, trimers, etc. [9], precludes a unique crossing point of the α_p isotherms.

A soft-sphere equation of state [12, 13] best reproduces the crossing point of α_p isotherms for unassociated liquids. For linearly associated liquids, such as 1-hexanol and its binary mixtures with *n*-hexane, encouraging

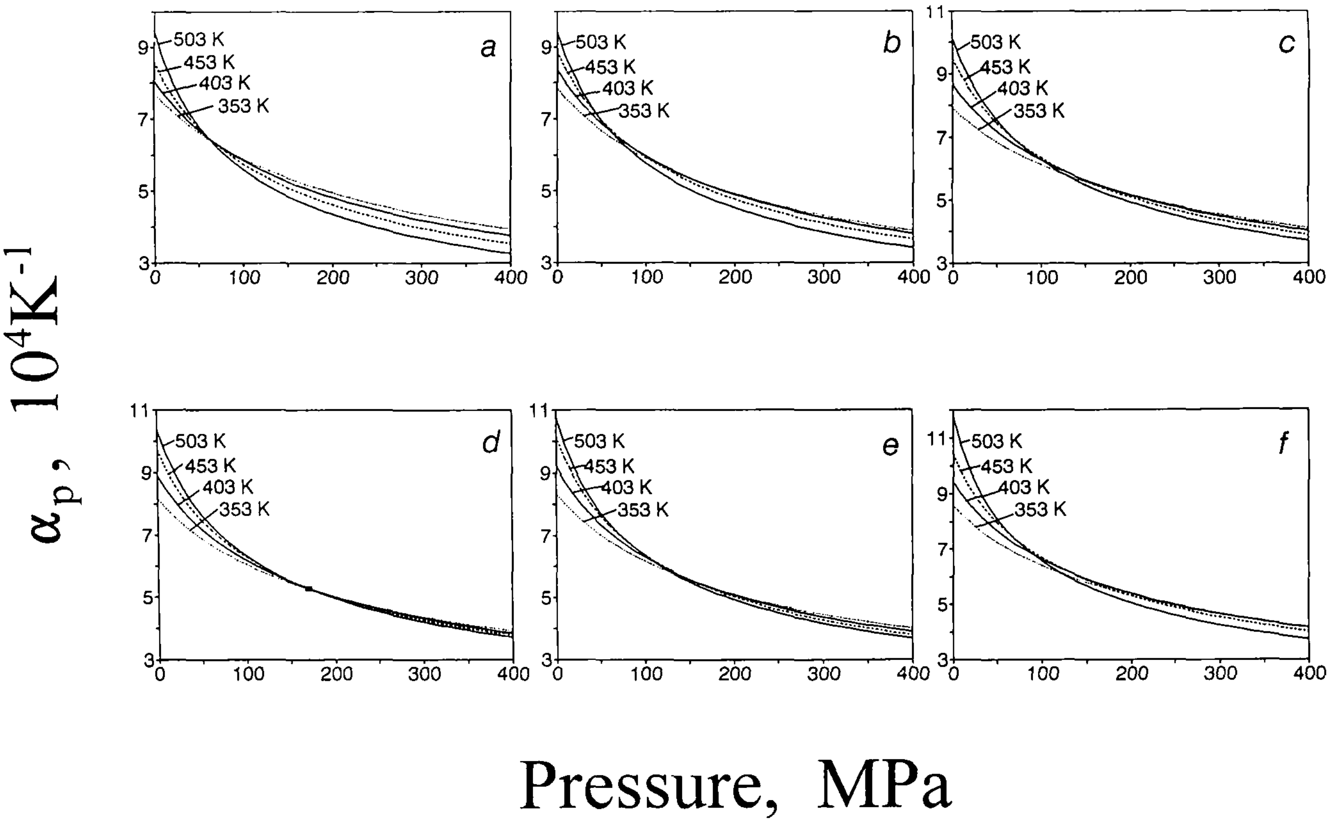

Fig. 1. *Selected isotherms of* α_p *for* (a) quinoline [8], (b) a {0.1499 *m*-cresol + 0.8501 quinoline} mixture, (c) a {0.5005 *m*-cresol + 0.4995 quinoline} mixture, (d) a {0.6325 *m*-cresol + 0.3675 quinoline} mixture, (e) a {0.8501 *m*-cresol + 0.1499 quinoline} mixture, and (f) *m*-cresol [7]. The unique crossing point of α_p isotherms for the {0.6325 *m*-cresol + 0.3675 quinoline} mixture (■) is at 170 MPa and $(5.27 \pm 0.01) \cdot 10^{-4}\ K^{-1}$].

results have been obtained with an additional term accounting for the linear association [14] added to the soft-sphere equation of state. No similar attempts have yet been made to describe the specific type of association between *m*-cresol and quinoline with an equation of state, but the behavior of $\alpha_p(p, T)$ for these mixtures cannot be described by any existing equation of state.

5. CONCLUSIONS

The isobaric thermal expansivities for five mixtures of *m*-cresol with quinoline have been measured with a pressure-controlled scanning calorimeter over the temperature range from 303 to 503 K at pressures up to 400 MPa, significantly extending existing literature data on the liquid phase of this system. The data are also presented as correlations equations. Near a 0.67 mol fraction of *m*-cresol the strong association of *m*-cresol with quinoline causes the liquid to behave like a simple liquid, exhibiting a unique crossing point of α_p isotherms. At lower and higher *m*-cresol concentrations the extent of intermolecular association is significantly affected by both pressure and temperature. The association equilibrium thus dominates the behavior of these mixtures. The data collected in this study contribute to a better understanding of the thermodynamic properties of coal liquids, especially the influence of pressure and temperature on those properties. Because the isobaric coefficient of thermal expansion is easily derived from equations of state, these data should also serve as an experimental base for further development of equations of state for associated systems.

ACKNOWLEDGMENT

S.L.R. wishes to express appreciation for the hospitality and financial support received from the Department of Chemistry and Biochemistry, Brigham Young University, during his visits there.

REFERENCES

1. S. L. Randzio, E. A. Lewis, D. J; Eatough, and L. D. Hansen, *Int. J. Thermophys.* **16**:883 (1995).
2. S. L. Randzio, E. A. Lewis, D. J; Eatough, and L. D. Hansen, *Int. J. Thermophys.* **17**:405 (1996).
3. S. L. Randzio, *Chem. Soc. Rev.* **24**:359 (1995).
4. 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).
5. S. L. Randzio, J.-P. E. Grolier, and J. R. Quint, *Fluid Phase Equil.* **110**:341 (1995).

6. S. L. Randzio, J.-P. E. Grolier, and J. R. Quint, *Int. J. Thermophys.* **18**:733 (1997).
7. D. J. Eatough, S. L. Wolfley, L. J. Dungan, E. A. Lewis, and L. D. Hansen, *J. Energy Fuels* **1**:94 (1987).
8. H. Tschamler and H. Krischai, *Monatsch. Chem.* **82**:259 (1951).
9. E. M. Woolley, J. G. Travers, B. O. Erno, and L. G. Hepler, *J. Phys. Chem.* **76**:359 (1971).
10. S. L. Randzio, D. J. Eatough, E. A. Lewis, and L. D. Hansen, *J. Chem. Thermodyn.* **20**:37 (1988).
11. S. L. Randzio, J.-P. E. Grolier, and J. R. Quint, *Rev. Sci. Instrum.* **65**:960 (1994).
12. U. K. Deiters and S. L. Randzio, *Fluid Phase Equil.* **103**:199 (1995).
13. S. L. Randzio and U. K. Deiters, *Ber. Bunsenges. Phys. Chem.* **99**:1179 (1995).
14. U. K. Deiters, *Fluid Phase Equil.* **89**:229 (1993).