Subscripts

CD	carbon dioxide
D	*n*-decane
HD	*n*-hexadecane

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Isothermal Compressibility of Cyclohexane + *n*-Hexane, Cyclohexane + *n*-Heptane, Cyclohexane + *n*-Octane, and Cyclohexane + *n*-Nonane

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The isothermal compressibility of cyclohexane + *n*-hexane, cyclohexane + *n*-heptane, cyclohexane + *n*-octane, and cyclohexane + *n*-nonane binary mixtures has been determined at 298.15, 308.15, 318.15, and 333.15 K. The "excess" function, $-V^{-1}(\partial V^E/\partial p)_T$, is negative for cyclohexane + *n*-hexane and cyclohexane + *n*-heptane systems, though the last one deviates only slightly from ideality. The "excess" function for the cyclohexane + *n*-nonane system is positive, while the cyclohexane + *n*-octane system is an ideal one. At 0.5 mole fraction the "excess" function absolute value of the cyclohexane + *n*-hexane system shows a maximum, which increases with temperature.

1. Introduction

Previous papers reported isothermal compressibility,[1] κ_T, molar excess enthalpy,[2,3] H^E, and molar excess volume,[4,5] V^E, for binary systems consisting of benzene + *n*-alkanes. In order to study the effect of aromaticity on certain excess functions, we determined compressibilities of similar systems containing cyclohexane instead of benzene. For these systems, both H^E and V^E were determined before.[6,7] We are in the process of finishing up compressibility measurements for the remaining members of the sequence. Thus we hope to make available a complete set of measurements on a regular sequence of binary systems which should prove useful for testing theoretical studies.

2. Experimental Section

Isothermal compressibility is usually defined as

$$\kappa_T = -V^{-1}(\partial V/\partial p)_T \qquad (1)$$

and the experimental technique used here for its determination was a piezometric method fully described before.[8-10] This procedure yields an error of less than 0.5%.

Table I gives information on the source and manufacturer reported purity of the chemicals. All chemicals were treated with sodium wire to eliminate moisture. The density of all substances was measured at every temperature. In our work the volume of any liquid on which compressibility was determined was always obtained through its mass and density. Our results at 298.15 K compare with those in the literature[11] reported in Table I. The procedure followed for mercury purification is given elsewhere.[10]

According to the relationship

$$V = x_1V_1 + x_2V_2 + V^E \qquad (2)$$

in order to calculate the liquid volume, one needs to know the excess volume. This one at 298.15 K for cyclohexane + *n*-hexane was determined by various authors[12-14] and their results agree with these of Sânchez Pajares and Nûñez Delgado,[7] who also measured V^E for cyclohexane + even *n*-alkanes at 298.15 K. The alkane C number of atoms went from 6 to 16. Those V^E values were used by us. Due to the small value of V^E, the correction applied to κ_T for the cyclohexane + *n*-nonane system (the one with the highest V^E) is less than 0.2%. On account of the smooth dependence of V^E on alkane chain length, we have obtained the V^E values for the odd alkane systems by interpolation. Some authors report a V^E decrease with temperature[12] for the cyclohexane + *n*-hexane system while others claim no change. In either case we are talking of less than 0.1% of the κ_T value. Therefore we have taken V^E to be temperature independent.

3. Results and Discussion

Isothermal compressibility of cyclohexane + *n*-hexane, cyclohexane + *n*-heptane, cyclohexane + *n*-octane, and cyclohexane + *n*-nonane systems were determined at negligible pressure and at 298.15, 308.15, 318.15, and 333.15 K.

Measurements on pure substances were run twice. Our results for cyclohexane are given in Table II, where literature data are included for comparison sake. A comparison of the experimental results for the remaining pure substances, *n*-hexane, *n*-heptane, *n*-octane, and *n*-nonane, with those in the literature is skipped here, as it was already made by us previously.[10]

Experimental κ_T results at various mole fractions are given in Table III.

The κ_T values as a function of cyclohexane mole fraction, x_1, were fitted to a polynomial of the type

$$\kappa_T/\mathrm{TPa}^{-1} = \sum_{i=0} A_i x_1^{\,i} \qquad (3)$$

where accordingly the pure substance κ_T value was assigned

Table I. Experimental Densities ρ at Various Temperatures and Comparison with Literature Data at 298.15 K and Mole Fraction Purity (x) of the Liquids

compd	source	10^2x	ρ/g·cm^{-3} exptl 298.15 K	exptl 308.15 K	exptl 318.15 K	exptl 333.15 K	lit.[a] 298.15 K
cyclohexane	Merck z.a.	≥99.5	0.773 92	0.764 51	0.754 85	0.740 36	0.773 89
n-hexane	Fluka puriss	≥99.5	0.655 13	0.646 07	0.636 79	0.622 21	0.654 81
n-heptane	Fluka puriss	≥99.5	0.679 81	0.671 21	0.662 61	0.649 31	0.679 51
n-octane	Merck z.s.	≥98	0.698 61	0.690 54	0.682 32	0.669 38	0.698 49
n-nonane	Fluka purum	≥99	0.714 35	0.706 57	0.698 47	0.686 33	0.713 81

[a] Reference 11.

Table II. Comparison of Cyclohexane Values with Literature Data

T/K	κ_T/TPa^{-1} this work	κ_T/TPa^{-1} literature
298.15	1120	1139,[a] 1135,[b] 1125,[c] 1130,[d] 1110,[e] 1130[f]
308.15	1219	1236,[a] 1214,[b] 1202[e]
318.15	1331	1342,[a] 1342,[b] 1315[e]
333.15	1520	1538,[a] 1520,[b] 1488[e]

[a] Interpolated from P, V measurements.[15] [b] From P, V measurements.[9] [c] From ultracentrifugal measurements.[16] [d] From P, V measurements.[17] [e] From P, V measurements.[8] [f] From ultrasonic velocity measurements.[18]

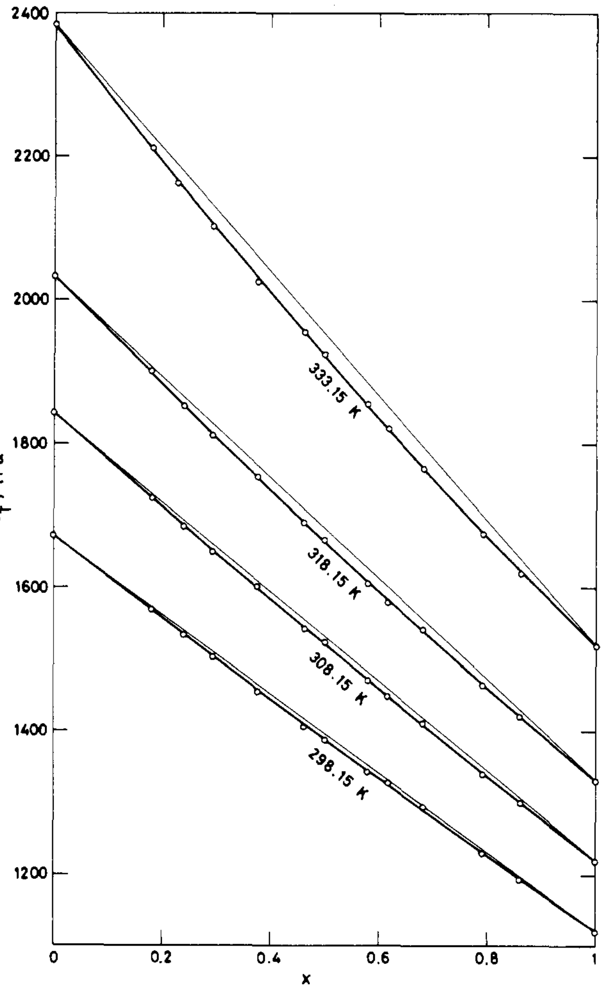

Figure 1. Isothermal compressibility κ_T against cyclohexane mole fraction x_1 for the cyclohexane + *n*-hexane system.

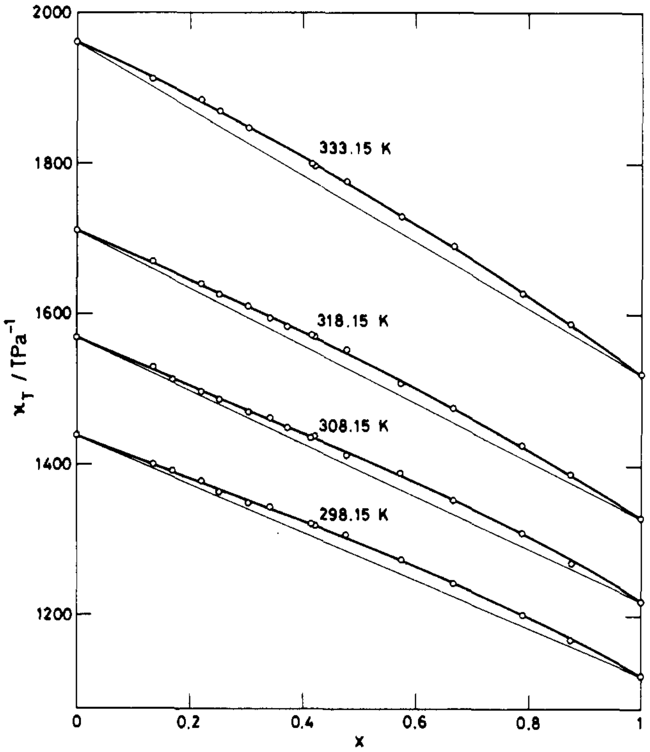

Figure 2. Isothermal compressibility κ_T against cyclohexane mole fraction x_1 for the cyclohexane + *n*-heptane system.

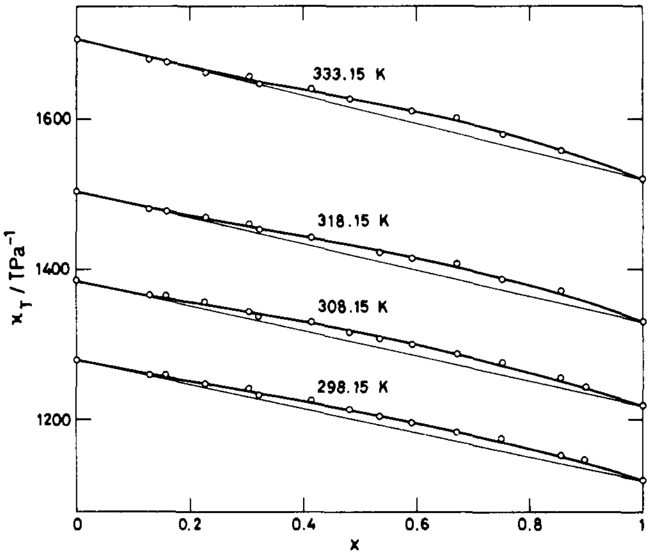

Figure 3. Isothermal compressibility κ_T against cyclohexane mole fraction x_1 for the cyclohexane + *n*-octane system.

double weight. The fit coefficients, A_i, and their standard deviation, σ, are given in Table IV.

On Figures 1-4 κ_T values vs. x_1 were plotted. The solid line curve corresponds to eq 3.

Differentiation of eq 2 with respect to pressure gives

$$(\partial V^E/\partial p)_T = (\partial V/\partial p)_T - x_1(\partial V_1/\partial p)_T - x_2(\partial V_2/\partial p)_T \quad (4)$$

Table III. Experimental Values of Isothermal Compressibility κ_T, $-V^{-1}(\partial V^E/\partial p)_T$, and $(\partial V^E/\partial p)_T$ at Negligible Pressures

x_1	κ_T/TPa^{-1}	$\kappa_T{}^E$/TPa^{-1}	$10^{-3}(\partial V^E/\partial p)_T$/ cm^3·mol^{-1}·TPa^{-1}	κ_T/TPa^{-1}	$\kappa_T{}^E$/TPa^{-1}	$10^{-3}(\partial V^E/\partial p)_T$/ cm^3·mol^{-1}·TPa^{-1}
	Cyclohexane (1) + *n*-Hexane (2)					
	T = 298.15 K			T = 308.15 K		
0	1672	0	0	1844	0	0
0.1818	1569	−17	1.8	1726	−20	2.6
0.2397	1538	−20	2.5	1685	−29	3.7
0.2935	1503	−27	3.4	1650	−33	4.2
0.3767	1455	−33	4.0	1602	−33	4.3
0.4630	1406	−35	4.2	1543	−40	4.9
0.5006	1388	−33	4.0	1524	−35	4.3
0.5803	1343	−34	4.0	1471	−38	4.6
0.6181	1329	−26	3.0	1449	−36	4.2
0.6819	1295	−23	2.6	1412	−31	3.7
0.7922	1231	−21	2.3	1341	−27	3.1
0.8613	1194	−15	1.7	1301	−19	2.1
1	1120	0	0	1219	0	0
	T = 318.15 K			T = 333.15 K		
0	2033	0	0	2384	0	0
0.1818	1902	−22	2.9	2212	−38	5.1
0.2397	1852	−35	4.6	2163	−53	7.0
0.2935	1811	−42	5.4	2102	−61	8.1
0.3767	1756	−43	5.4	2026	−70	9.1
0.4630	1691	−49	6.1	1956	−69	8.7
0.5006	1667	−47	5.8	1924	−68	8.6
0.5803	1606	−52	6.3	1856	−67	8.3
0.6181	1579	−51	6.2	1822	−67	8.3
0.6819	1542	−41	4.9	1765	−66	8.0
0.7922	1464	−35	4.1	1676	−52	6.2
0.8613	1420	−25	2.9	1621	−39	4.6
1	1331	0	0	1520	0	0
	Cyclohexane (1) + *n*-Heptane (2)					
	T = 298.15 K			T = 308.15 K		
0	1440	0	0	1569	0	0
0.1345	1401	−5	0.7	1529	−2	0.4
0.1699	1393	−4	0.6	1513	−9	1.2
0.2209	1379	−4	0.6	1497	−10	1.4
0.2525	1365	−9	1.3	1487	−10	1.4
0.3043	1351	−9	1.2	1471	−10	1.4
0.3421	1345	−4	0.6	1463	−6	0.8
0.3732				1449	−11	1.4
0.4169	1324	−3	0.4	1436	−9	1.2
0.4222	1321	−4	0.5	1439	−4	0.6
0.4780	1308	−1	0.1	1413	−12	1.5
0.5745	1275	−2	0.2	1390	−1	0.1
0.6665	1243	−3	0.4	1354	−3	0.4
0.7903	1202	0	0.0	1311	2	−0.2
0.8757	1168	−2	0.2	1271	−3	0.3
1	1120	0	0	1219	0	0
	T = 318.15 K			T = 333.15 K		
0	1712	0	0	1962	0	0
0.1345	1670	−2	0.3	1913	−2	0.3
0.2209	1641	−3	0.4	1885	2	−0.3
0.2525	1626	−8	1.2	1871	0	0.0
0.3043	1610	−6	0.9	1848	−3	0.4
0.3421	1595	−9	1.2			
0.3732	1583	−10	1.4			
0.4169	1573	−4	0.6	1799	−7	0.9
0.4222	1570	−6	0.8	1797	−7	0.9
0.4780	1552	−4	0.5	1777	−3	0.5
0.5745	1508	−11	1.3	1729	−9	1.1
0.6665	1475	−7	0.8	1690	−5	0.6
0.7903	1427	−2	0.2	1627	−7	0.8
0.8757	1388	−3	0.3	1587	−3	0.3
1	1331	0	0	1520	0	0
	Cyclohexane (1) + *n*-Octane (2)					
	T = 298.15 K			T = 308.15 K		
0	1280	0	0	1386	0	0
0.1280	1260	−5	0.8	1366	−4	0.7
0.1586	1261	0	0.0	1366	0	0.0
0.2265	1248	−4	0.6	1357	−1	0.1
0.3049	1242	0	−0.1	1344	−2	0.3

Table III (*Continued*)

x_1	κ_T/TPa^{-1}	κ_T^E/TPa^{-1}	$10^{-3}(\partial V^E/\partial p)_T$/ cm^3·mol^{-1}·TPa^{-1}	κ_T/TPa^{-1}	κ_T^E/TPa^{-1}	$10^{-3}(\partial V^E/\partial p)_T$/ cm^3·mol^{-1}·TPa^{-1}
			Cyclohexane (1) + *n*-Octane (2)			
		T = 298.15 K			T = 308.15 K	
0.3224	1233	−6	0.9	1337	−7	1.0
0.4145	1227	1	−0.1	1330	1	−0.1
0.4828	1214	−1	0.1	1316	−3	0.4
0.5356	1205	−2	0.3	1308	−2	0.3
0.5918	1196	−2	0.3	1300	−1	0.1
0.6722	1184	0	0.0	1287	1	−0.1
0.7522	1175	5	−0.7	1277	6	−0.7
0.8558	1153	4	0.0	1256	6	−0.7
0.8981	1148	7	−0.8	1244	3	−0.3
1	1120	0	0	1219	0	0
		T = 318.15 K			T = 333.15 K	
0	1504	0	0	1707	0	0
0.1280	1480	−8	1.3	1680	−9	1.5
0.1586	1477	−7	1.0	1676	−8	1.3
0.2265	1469	−5	0.7	1663	−11	1.7
0.3049	1461	−1	0.2	1657	−5	0.7
0.3224	1453	−7	1.0	1648	−11	1.6
0.4145	1443	−2	0.3	1641	−2	0.3
0.4828				1628	−3	0.4
0.5356	1422	−3	0.4			
0.5918	1415	0	0.0	1612	2	−0.2
0.6722	1408	8	−1.1	1602	8	−1.0
0.7522	1387	2	−0.3	1580	2	−0.3
0.8558	1373	9	−1.1	1558	3	−0.4
1	1331	0	0	1520	0	0
			Cyclohexane (1) + *n*-Nonane (2)			
		T = 298.15 K			T = 308.15 K	
0	1177	0	0	1268	0	0
0.1737	1173	3	−0.6	1272	11	−1.8
0.2517	1175	9	−1.5	1266	9	−1.4
0.3396	1175	14	−2.2	1270	16	−2.6
0.3531	1173	13	−2.0	1270	17	−2.7
0.4176	1167	11	−1.6	1261	12	−1.8
0.5037	1161	9	−1.3	1257	12	−1.7
0.5250	1161	11	−1.5	1256	12	−1.7
0.5811	1161	14	−2.0	1256	15	−2.1
0.6937	1153	13	−1.7	1250	14	−1.9
0.7532	1148	11	−1.4	1241	9	−1.1
0.8028	1147	14	−1.7	1242	12	−1.6
0.8751	1136	8	−1.0	1236	10	−0.7
1	1120	0	0	1219	0	0
		T = 318.15 K			T = 333.15 K	
0	1366	0	0	1533	0	0
0.1737	1370	10	−1.7	1538	8	−1.5
0.2517	1368	10	−1.7	1538	9	−1.6
0.3396	1368	13	−2.2	1540	13	−2.2
0.3531	1363	9	−1.4	1535	9	−1.4
0.4176	1368	16	−2.5	1540	14	−2.2
0.5037	1364	16	−2.3	1535	11	−1.7
0.5250	1364	16	−2.4	1538	15	−2.2
0.5811	1366	21	−2.9	1541	19	−2.7
0.6937	1358	17	−2.2	1538	17	−2.4
0.7532	1354	15	−1.9	1532	12	−1.5
0.8028	1350	13	−1.6			
0.8751	1345	10	−1.5	1525	6	−1.0
1	1331	0	0	1520	0	0

where $(\partial V^E/\partial p)_T$ is the difference between values for the real and the ideal systems. This difference is the usually defined excess function and is preferred by some authors.[19] Its values are given in Table III.

Nevertheless most authors[20,21] use the excess function as defined by

$$\kappa_T^E = -V^{-1}(\partial V^E/\partial p)_T = \kappa_T - \phi_1\kappa_{1T} - \phi_2\kappa_{2T} \qquad (5)$$

where ϕ_i is the volume fraction

$$\phi_i = x_iV_i/V \qquad (6)$$

and V is obtained from eq 2.

It will be noticed that this "excess" function is negative for the cyclohexane + n-hexane and cyclohexane + n-heptane systems and positive for cyclohexane + n-nonane. None of the κ_T curves on Figures 1–4 coincide with the straight line joining the pure substances compressibility, while from the data in Table III it will be noticed that the cyclohexane + n-octane system is ideal. The straight line does not represent an ideal system and the eq 5 definition of κ_T^E does not agree with the usual excess function definition.

The κ_T^E values given in Table III for the cyclohexane +

Table IV. Coefficients and Standard Deviation $\sigma(\kappa_T)$ for the Adjustment of κ_T According to Equation 3

T/K	A_0	A_1	A_2	A_3	$\sigma(\kappa_T$/TPa$^{-1})$
		Cyclohexane (1) + n-Hexane (2)			
298.15	1672.3	−580.4	28.7		2.9
308.15	1843.7	−662.1	37.4		1.8
318.15	2034.7	−774.0	69.8		2.7
333.15	2384.1	−987.3	122.1		2.8
		Cyclohexane (1) + n-Heptane (2)			
298.15	1439.9	−288.4	48.0	−80.5	1.9
308.15	1569.5	−340.1	102.7	−113.6	2.6
318.15	1712.4	−328.6	−14.9	−38.6	2.2
333.15	1961.8	−335.2	−127.4	21.3	1.9
		Cyclohexane (1) + n-Octane (2)			
298.15	1280.5	−150.8	64.6	−73.3	2.4
308.15	1387.0	−158.8	69.5	−77.8	2.2
318.15	1503.9	−186.1	144.0	−130.0	2.7
333.15	1706.1	−214.7	190.1	−162.1	2.2
		Cyclohexane (1) + n-Nonane (2)			
298.15	1177.2	−9.5	−12.1	−35.3	2.1
308.15	1268.6	18.6	−73.6	6.4	2.5
318.15	1366.4	6.7	5.9	−47.9	1.8
333.15	1533.4	21.8	−11.7	−24.0	2.2

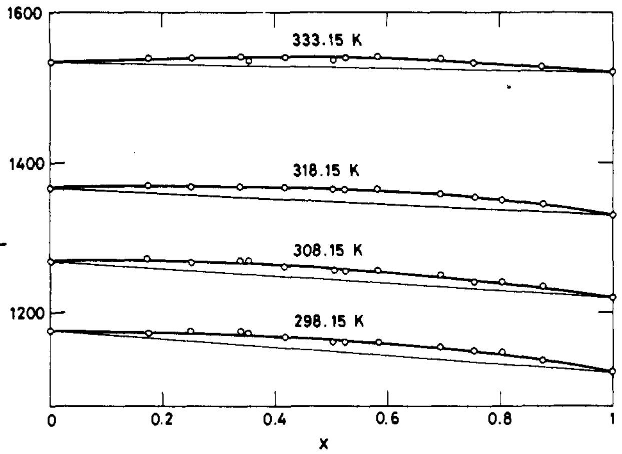

Figure 4. Isothermal compressibility κ_T against cyclohexane mole fraction x_1 for the cyclohexane + n-nonane system.

n-hexane, cyclohexane + n-heptane, and cyclohexane + n-nonane systems were fitted to a polynomial of the type

$$\kappa_T^E = x_1x_2\{B_0 + (2x_1 - 1)B_1\} \tag{7}$$

whose coefficients and standard deviations are given in Table V. No fit has been sought for the cyclohexane + n-octane system since it is an ideal one.

The κ_T^E values obtained from eq 7 were plotted against the cyclohexane mole fraction on Figure 5. Here we notice that the κ_T^E numerical value changes its sign between the cyclohexane + n-heptane and cyclohexane + n-nonane systems. This change also occurs in the benzene + n-alkane sequence going from a negative value for benzene + n-hexane to a somewhat larger than zero value for the benzene + n-heptane system. On both series V^E is always positive.

One observes on Figure 5 that the absolute value of κ_T^E shows a maximum at $x_1 = 0.5$. The absolute value of κ_T^E for the cyclohexane + n-hexane system increases with temperature. A corresponding change for the cyclohexane + n-heptane and cyclohexane + n-nonane systems, if it exists, is within the experimental error. For the cyclohexane + n-heptane system, κ_T^E in the maximum region amounts to less than 1% of the mixture κ_T value.

Table V. Coefficients and Standard Deviation $\sigma(\kappa_T^E)$ for the Adjustment of κ_T^E According to Equation 7

T/K	B_0	B_1	$\sigma(\kappa_T^E$/TPa$^{-1})$
	Cyclohexane (1) + n-Hexane (2)		
298.15	−124.6	1.3	2.8
308.15	−152.0	−6.1	1.9
318.15	−195.2	−26.6	2.8
333.15	−291.5	−26.0	3.2
	Cyclohexane (1) + n-Heptane (2)		
298.15	−18.5	22.4	2.1
308.15	−28.0	29.8	2.8
318.15	−27.2	1.7	2.3
333.15	−21.1	−22.5	2.0
	Cyclohexane (1) + n-Nonane (2)		
298.15	54.0	28.1	2.4
308.15	62.7	9.4	2.9
318.15	67.8	26.1	1.9
333.15	58.5	10.1	2.5

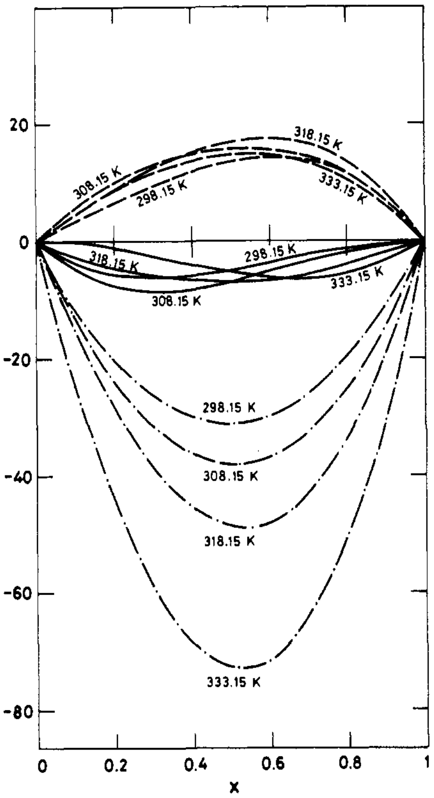

Figure 5. Plot of κ_T^E against cyclohexane mole fraction x_1: (– – –) cyclohexane + n-nonane; (—) cyclohexane + n-heptane; (– • – •) cyclohexane + n-hexane.

Glossary

A_1, A_2, ..., A_i	coefficients in representation of isothermal compressibility by eq 3
B_0, B_1	coefficients in representation of excess compressibility by eq 7
H^E	molar excess enthalpy, J·mol^{-1}
P	pressure, TPa^{-1}
T	temperature, K
V	molar volume, cm^3·mol^{-1}
V^E	molar excess volume, cm^3·mol^{-1}
x_i	mole fraction of component i

Greek Letters

ϕ_i	volume fraction
κ_T	isothermal compressibility, TPa^{-1}
κ_T^E	excess compressibility, TPa^{-1}
ρ	density, g·cm^{-3}

σ standard deviation

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Vapor–Liquid Equilibrium in Binary Mixtures of Carbon Dioxide + Diphenylmethane and Carbon Dioxide + 1-Methylnaphthalene

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Vapor–liquid equilibrium data for binary mixtures of carbon dioxide with diphenylmethane and with 1-methylnaphthalene are determined at temperatures between 189 and 430 °C and at pressures between 20 and 50 atm.

Introduction

Carbon dioxide is an important nonhydrocarbon component in petroleum reservoir fluids and natural gases and is encountered in coal conversion processes. Phase equilibrium data on carbon dioxide mixtures are, therefore, of considerable industrial and engineering interest. We (*5*) recently reported vapor–liquid equilibrium data in binary mixtures of carbon dioxide + *n*-decane and carbon dioxide + *n*-hexadecane and reviewed the literature on carbon dioxide + heavy paraffins. In this work we report the compositions of saturated equilibrium liquid and vapor phases for binary mixtures of carbon dioxide + diphenylmethane and carbon dioxide + 1-methylnaphthalene at temperatures between 189 and 430 °C and at pressures between 20 and 50 atm.

No phase equilibrium data have been previously reported for these two binary systems at the temperature and pressures of this work. Tremper and Prausnitz (*9*) measured low-pressure solubilities up to 200 °C. A few other studies have been reported on mixtures of CO_2 with aromatic hydrocarbons but all were limited to temperatures below those of this work. Ng and Robinson (*3*) reported data for carbon dioxide + toluene mixtures at 38–204 °C and at pressures up to 151 atm. Ohgaki and Katayama (*4*) and Wan and Dodge (*10*) determined solubility of CO_2 in benzene at temperatures up to 60 °C. Luks and Kohn and co-workers (*2*, *8*, *11*) studied binary mixtures of carbon dioxide + 2-methylnaphthalene and carbon dioxide + butylbenzene at low temperatures and ternary mixtures of carbon dioxide + *n*-decane + 2-methylnaphthalene and carbon dioxide + butylbenzene + 2-methylnaphthalene. Francis (*1*) measured solubilities of CO_2 in aromatic compounds at 25 °C.

Table I. Carbon Dioxide + Diphenylmethane Vapor–Liquid Equilibrium Data

p, atm	x_{CD}	y_{CD}	K_{CD}	K_D
		189.6 °C		
18.90	0.0572	0.9886	17.28	0.0121
19.84	0.0594	0.9892	16.65	0.0115
29.69	0.0876	0.9921	11.33	0.00866
40.1	0.1163	0.9933	8.541	0.00758
49.6	0.1429	0.9938	6.955	0.00723
		269.4 °C		
20.17	0.0512	0.9329	18.22	0.0707
30.01	0.0777	0.9505	12.23	0.0537
39.8	0.1017	0.9582	9.422	0.0465
50.3	0.1283	0.9634	7.509	0.0420
		350.2 °C		
19.17	0.0394	0.7127	18.09	0.2991
30.67	0.0684	0.7999	11.69	0.2148
40.0	0.0925	0.8338	9.014	0.1831
49.4	0.1155	0.8567	7.417	0.1621
		430.6 °C		
29.45	0.0505	0.4303	8.521	0.6000
40.2	0.0818	0.5312	6.494	0.5106
50.0	0.1127	0.5915	5.249	0.4604

Experimental Section

The apparatus and procedure used in this study have been described previously by Simnick et al. (*6*). A minor change has been made in the apparatus with the addition of a Heise gauge (Model CMM) which measures pressures below 34 atm to an increased accuracy of ±0.03 atm.

The apparatus is of the flow type to minimize thermal decomposition of the hydrocarbons at high temperatures. The

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