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Vapor–Liquid Equilibrium in Binary Mixtures of Carbon Dioxide + *n*-Decane and Carbon Dioxide + *n*-Hexadecane

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Compositions of saturated vapor and liquid at equilibrium were experimentally determined at four temperatures from 190 to 310 °C for carbon dioxide + *n*-decane and from 190 to 390 °C for carbon dioxide + *n*-hexadecane. Measurements were made at four pressures from 20 to 50 atm at each temperature for both systems.

Introduction

Carbon dioxide is an important nonhydrocarbon component in petroleum reservior fluids and natural gases. Significant quantities of CO_2 are also found in coal conversion processes. Phase equilibria in CO_2 mixtures have been studied by a number of investigators. Kulkarni and co-workers (*2*) reviewed binary systems of CO_2 with heavy paraffins, including *n*-decane and *n*-hexadecane, and reported equilibrium data on carbon dioxide + *n*-decane. Their data and the data reviewed were at low temperatures, except for the work of Reamer and Sage (*3*), who determined the equilibrium compositions of gas and liquid phases for the carbon dioxide + *n*-decane system at temperatures from 4.4 to 238 °C and at pressures up to 680 atm. Solubility data for CO_2 in *n*-hexadecane at temperatures above room temperature are available from several studies (*1*, *4*, *6*), but only the liquid-phase compositions at low pressures were reported.

In this work we observed the saturated fluid phases of carbon dioxide *n*-decane and carbon dioxide + *n*-hexadecane systems at four temperatures from 190 to 310 °C for the first system and from 190 to 390 °C for the second. Pressure was in the range of 20–50 atm.

Experimental Section

A flow-type apparatus was used in this work. A detailed description of the apparatus and the experimental procedure was given by Simnick and co-workers (*5*). This work departed from the description given there in a minor way in that the gas compressor was bypassed. Carbon dioxide gas was supplied to the system directly from the cylinder as purchased. Furthermore, a Model CMM Heise gauge, which reads pressures up to 34 atm with an accuracy of ±0.03 atm, was added to the system for improved accuracy at low pressures.

Carbon dioxide was purchased from Matheson with a minimum purity of 99.99% (Coleman Instrument grade). *n*-Decane used in this study was Gold Label grade purchased from Aldrich Chemical Co. and *n*-hexadecane was supplied by Matheson Coleman and Bell Co. Both were claimed to have 99+% purity.

Condensate from the overhead cell effluent and the bottom effluent were sampled at each experimental condition for analysis by gas chromatography. No decomposition products were found at any of the conditions studied. Nevertheless, the cell effluents were purified by distillation under a reduced nitrogen atmosphere before being reused.

Table I. Vapor-Liquid Equilibrium Data for Carbon Dioxide + *n*-Decane

p, atm	x_{CD}	y_{CD}	K_{CD}	K_D
		189.4 °C		
19.36	0.0913	0.9075	9.939	0.1018
30.38	0.1472	0.9306	6.322	0.0814
40.1	0.1883	0.9410	4.997	0.0727
50.7	0.2358	0.9478	4.020	0.0683
		203.8 °C		
14.25	0.0635	0.8340	13.134	0.1773
27.11	0.1239	0.8966	7.236	0.1180
40.8	0.1872	0.9240	4.936	0.0935
50.1	0.2282	0.9303	4.077	0.0903
		269.8 °C		
19.38	0.0656	0.5700	8.689	0.4602
29.63	0.1147	0.6818	5.944	0.3594
39.5	0.1628	0.7357	4.519	0.3157
51.0	0.2145	0.7655	3.568	0.2985
		310.5 °C		
19.76	0.0427	0.2489	5.829	0.7846
30.00	0.0974	0.4115	4.225	0.6520
40.5	0.1558	0.5015	3.219	0.5905
50.4	0.2125	0.5419	2.550	0.5817

Table II. Vapor-Liquid Equilibrium Data for Carbon Dioxide + *n*-Hexadecane

p, atm	x_{CD}	y_{CD}	K_{CD}	K_{HD}
		189.9 °C		
19.80	0.1091	0.9953	9.123	0.0053
29.95	0.1629	0.9955	6.111	0.0054
40.7	0.2162	0.9953	4.604	0.0060
50.1	0.2575	0.9953	3.865	0.0063
		269.7 °C		
19.83	0.0990	0.9573	9.670	0.0474
29.87	0.1462	0.9681	6.622	0.0374
40.5	0.1934	0.9729	5.031	0.0336
50.2	0.2321	0.9759	4.205	0.0314
		350.4 °C		
19.96	0.0912	0.7860	8.618	0.2355
29.91	0.1421	0.8427	5.930	0.1834
39.9	0.1898	0.8688	4.577	0.1619
50.0	0.2350	0.8837	3.760	0.1520
		390.6 °C		
20.60	0.0897	0.6019	6.710	0.4373
30.03	0.1423	0.6926	4.867	0.3584
40.0	0.1957	0.7400	3.781	0.3233
50.0	0.2478	0.7682	3.100	0.3082

Fluctuations of the equilibrium cell temperature during the measurement of all the points on an isotherm were within 0.11 °C at the three lower isotherms and within 0.25 °C at the highest isotherm for the carbon dioxide + *n*-decane system and were within 0.11 °C for all the isotherms of carbon dioxide + *n*-hexadecane.

Attainment of equilibrium in the flow apparatus of this work was verified by varying the flow rate of the feeds. A variation of the liquid feed from 18 to 32 mL/min produced no appreciable change in the observed intensive variables. Another verification of equilibrium is the agreement of our data on carbon dioxide + *n*-decane with those of Reamer and Sage (*3*) determined in a static apparatus. This agreement will be discussed in the next section.

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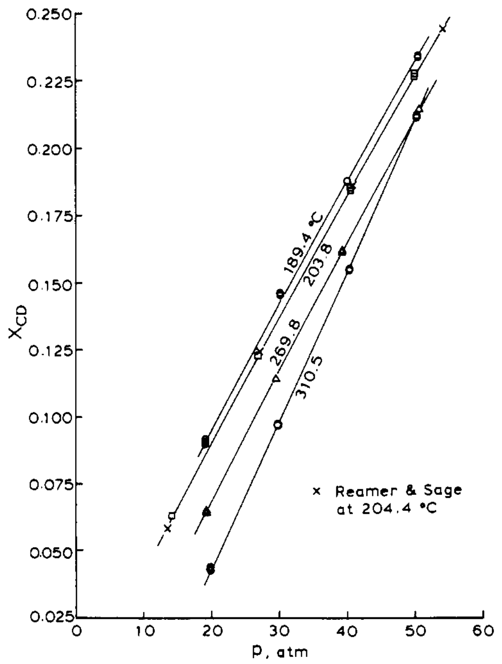

Figure 1. Solubility of carbon dioxide in *n*-decane.

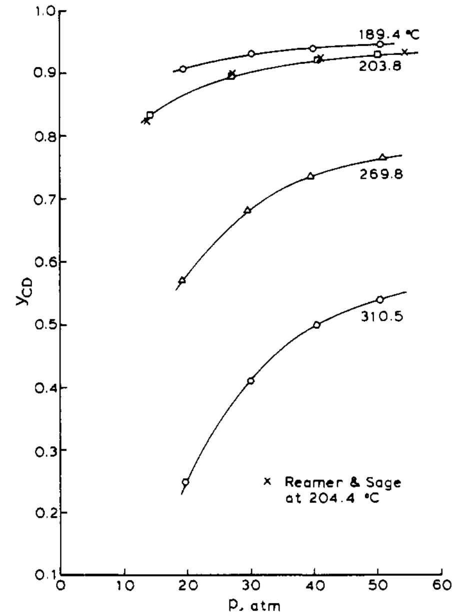

Figure 2. Mole fraction of carbon dioxide in saturated vapor in carbon dioxide + *n*-decane.

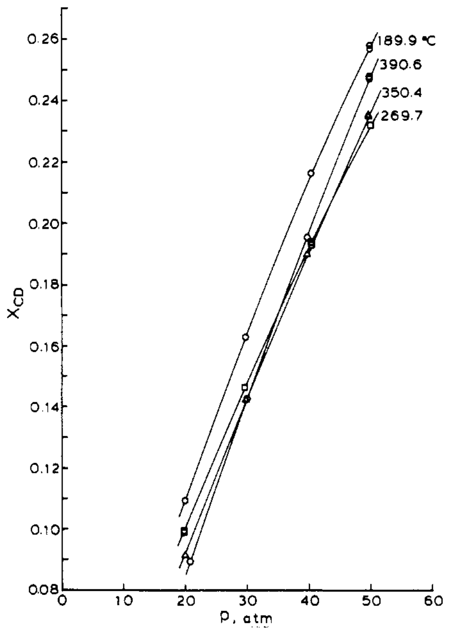

Figure 3. Solubility of carbon dioxide in *n*-hexadecane.

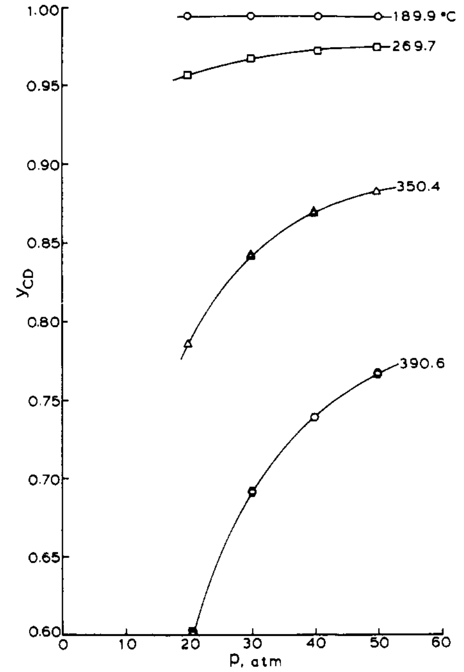

Figure 4. Mole fraction of carbon dioxide in saturated vapor in carbon dioxide + *n*-hexadecane.

Results and Discussion

Experimental results are presented in Table I for carbon dioxide + *n*-decane and Table II for carbon dioxide + *n*-hexadecane. The saturated compositions reported in the tables are the mean values from multiple samples which, in general, agree to within 1% of the mole fraction value at each condition of temperature and pressure. These mean values were then used to calculate the vaporization equilibrium ratios.

Figures 1 and 2 show the isothermal vapor and liquid equilibrium phase compositions respectively as a function of pressure for carbon dioxide + *n*-decane. The individual sample points are indicated in the figures when they can be distinguished. Isothermal compositions for carbon dioxide + *n*-hexadecane are similarly shown in Figures 3 and 4.

Our data on carbon dioxide + *n*-decane represent an extension of those of Reamer and Sage to higher temperatures. There is a small temperature range of intersection from 189.4 °C, which is our lowest temperature, to 238 °C, which is their highest. In Figures 1 and 2 we show their data at 204.4 °C. These practically coincide with ours at 203.8 °C. The resolution of the figure is insufficient to differentiate between the two isotherms at their slightly different temperatures. The two sets of data appear to be in excellent agreement and merge smoothly at the intersection.

Acknowledgment

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Glossary

K	vaporization equilibrium ratio, y/x
p	pressure, atm
t	temperature, °C
x	mole fraction in liquid phase
y	mole fraction in vapor phase

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

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

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

$$V = x_1V_1 + x_2V_2 + V^E \tag{2}$$

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 Sánchez Pajares and Núñez 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

$$\kappa_T/\text{TPa}^{-1} = \sum_{i=0} A_i x_1^{\,i} \tag{3}$$

where accordingly the pure substance κ_T value was assigned

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