$$\ln \gamma_n = S\frac{(2x_1 - 1)}{1 - x_1} + x_1 W - \frac{x_1^2}{1 - x_1}(1 - Z)\ln(1 - x_1)\sum_{i\neq 1,n}^{m} x_i(A_i - A_n) + x_1 C_n - x_1\sum_{i=2}^{m} x_i C_i + \sum_{j=2}^{m}[2\Lambda_{nj}x_n x_j(1 - x_n) + x_j^2\Lambda_{jn}(1 - 2x_n)]_{(j\neq n)} - 2\sum_{j=3}^{m}\sum_{i=2}^{m}(x_i^2 x_j \Lambda_{ij} + x_j^2 x_i \Lambda_{ji})_{i,j\neq n} \qquad \text{(A4)}$$

where S, W, and Z are defined above and

$$A = \sum_{i=2}^{m}\frac{A_i x_i}{\sum_{2}^{m} x_i}$$

Registry No. DMF, 68-12-2; ethanol, 64-17-5.

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Equilibrium Phase Compositions, Phase Densities, and Interfacial Tensions for CO_2 + Hydrocarbon Systems. 3. CO_2 + Cyclohexane. 4. CO_2 + Benzene

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Experimental vapor–liquid equilibrium phase compositions, phase densities, and interfacial tensions are presented for CO_2 + cyclohexane and for CO_2 + benzene at 160 °F at pressures from 1000 psia to the critical point (interfacial tensions as low as 0.009 mN/m). These data for CO_2 with a naphthenic and an aromatic hydrocarbon complement our earlier work on binary mixtures of CO_2 with the paraffins *n*-butane and *n*-decane.

Introduction

The work presented here on CO_2 + cyclohexane and CO_2 + benzene is the third in a planned series of studies on CO_2 + hydrocarbon systems which will include measurements on CO_2 with other pure and mixed hydrocarbons and with reservoir oils. The previous two parts of this series presented data on CO_2 + *n*-butane (*1*) and CO_2 + *n*-decane (*2*). These new data on interfacial tensions (IFT) in CO_2 + hydrocarbon systems provide additional information on the effects of temperature, pressure, and composition on the IFT in such systems, which could lead to improved understanding of the process of miscible (or near-miscible, low-IFT) displacement of reservoir oils by CO_2 injection.

Experimental Method

The apparatus and procedures used in the present measurements have been described in detail previously (*1*, *2*). The only change in procedures from those used in the study of CO_2 + *n*-decane involved the chromatographic analysis of compositions, where 10 ft of 0V101 at 170 °C was used to separate CO_2 from cyclohexane or benzene. Response factors of 0.553 and 0.609 were used in the analyses of the cyclohexane and benzene systems, respectively, based on volumetrically prepared calibration mixtures.

Table I. Pure Component Equilibrium Phase Properties at 160 °F

vapor pressure, psia	phase densities, (kg/m^3) × 10^{-3} liquid	vapor	ref
	Cyclohexane		
11.0	0.7282	0.0038	this work
10.9	0.7294		*3*, *4*
	Benzene		
11.0	0.8225	0.0042	this work
11.0	0.8237	0.0021	*3*, *4*

Materials

The CO_2 was supplied by Union Carbide Linde Division and had a stated purity of 99.99%. The cyclohexane and benzene were from Phillips Petroleum Co. (Research Grade) with purities of 99.9%. The chemicals were used without further purification.

Experimental Results

The complete data appear in Tables I–III. As part of the measurements, phase compositions and densities of pure cyclohexane and benzene were measured. They are compared in Table I with values interpolated from the literature (*3*, *4*).

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Table II. Phase Equilibria and Interfacial Tensions at 344.3 K (160 °F)

pressure		phase comp, mole fraction CO_2		phase densities, $(kg/m^3) \times 10^{-3}$		interfacial tension, mN/m
kPa	psia	liquid	vapor	liquid	vapor	
			CO_2 + Cyclohexane			
6870	997	0.426	0.952	0.7348	0.1493	6.35
7590	1101	0.481	0.947	0.7336	0.1760	4.98
8270	1200	0.534	0.949	0.7309	0.2054	3.71
8960	1300	0.596	0.946	0.7248	0.2341	2.62
9650	1400	0.665	0.940	0.7119	0.2785	1.39
9995	1450	0.704	0.935	0.7005	0.3044	0.947
10340	1500	0.747	0.927	0.6796	0.3375	0.519
10510	1525	0.766	0.923	0.6658	0.3592	0.365
10620	1540	0.781	0.920	0.6553	0.3756	0.254
10690	1550	0.792	0.916	0.6451	0.3876	0.180
10760	1560	0.803	0.913	0.6353	0.4011	0.135
10820	1570	0.815	0.908	0.6198	0.4170	0.081
10890	1579	0.826	0.901	0.6058	0.4396	0.036
10930	1586	0.840	0.896	0.5822	0.4680	0.009
10960[a]	1589	0.848	0.883	0.5683	0.4987	
10970[b]	1590	0.880		0.5250		
			CO_2 + Benzene			
6895	1000	0.453	0.932	0.8150	0.1560	6.60
7590	1101	0.507	0.937	0.8095	0.1775	4.96
8280	1201	0.564	0.941	0.8012	0.2048	3.72
8960	1300	0.625	0.940	0.7875	0.2374	2.48
9645	1399	0.692	0.936	0.7636	0.2786	1.39
9855	1430	0.712	0.934	0.7503	0.2952	1.10
9995	1450	0.726	0.932	0.7403	0.3061	0.917
10170	1475	0.745	0.929	0.7312	0.3223	0.709
10340	1500	0.763	0.925	0.7141	0.3413	0.508
10480	1520	0.779	0.924	0.6977	0.3577	0.363
10580	1535	0.793	0.919	0.6853	0.3744	0.262
10690	1550	0.805	0.916	0.6692	0.3910	0.172
10750	1559	0.815	0.912	0.6578	0.4064	0.123
10830	1571	0.828	0.907	0.6376	0.4275	0.065
10890	1580	0.841	0.902	0.6167	0.4500	0.026
10920	1584	0.846	0.898	0.5996	0.4642	0.011
10960[b]	1589	0.875		0.5330		

[a] Suspect data point. [b] Estimated critical point.

Table III. Critical Properties at 160 °F

press., psia	density, $(kg/m^3) \times 10^{-3}$	composition, mole fraction CO_2	ref
	CO_2 + Cyclohexane		
1590	0.525	0.880	this work
[a]	0.515	0.91	*7*
	CO_2 + Benzene		
1589	0.533	0.875	this work
1590	[b]	0.889	*10*

[a] Critical pressures could not be interpolated accurately. [b] Critical density was not measured.

Interfacial tensions for the pure substances were not determined because they were too high to be measured accurately in the present apparatus. The mixture phase densities, compositions, and interfacial tensions are given in Table II. The data are illustrated in Figures 1-3 for CO_2 + cycohexane; results for CO_2 + benzene are qualitatively similar.

No previous data are available for direct comparison with the present mixture data. However, Anderson et al. (*5*) performed measurements of phase compositions for CO_2 + cyclohexane at 167 °F. Their data (adjusted to 160 °F by using a suitable equation of state) agree with the present results to within approximately 0.002 mole fraction at 1000 psia, with differences rising to 0.009 at 1300 psia (the range of ovelap in the two data sets). Krichevskii and Sorina (*6*, *7*) have also measured phase equilibria for CO_2 + cyclohexane, but not at 160 °F. Their data have been interpolated to yield values of the critical density and composition at 160 °F and are in reasonable agreement with the present results (Table III). Their critical pressure locus could not be interpolated with enough accuracy to permit

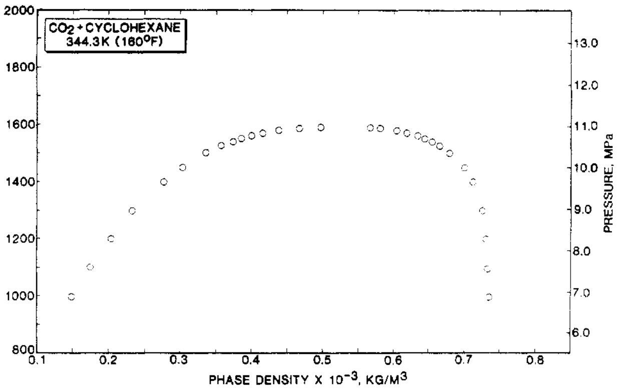

Figure 1. Phase densities for CO_2 + cyclohexane at 160 °F.

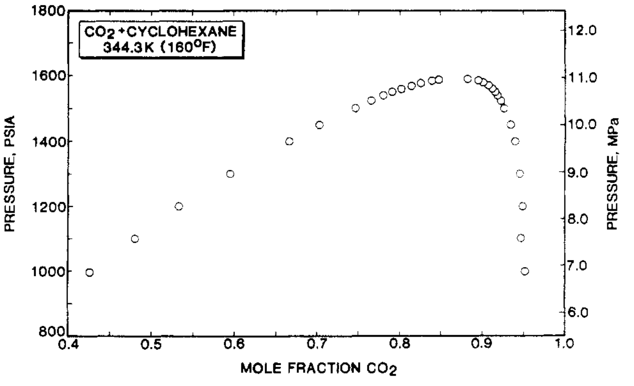

Figure 2. Phase compositions for CO_2 + cyclohexane at 160 °F.

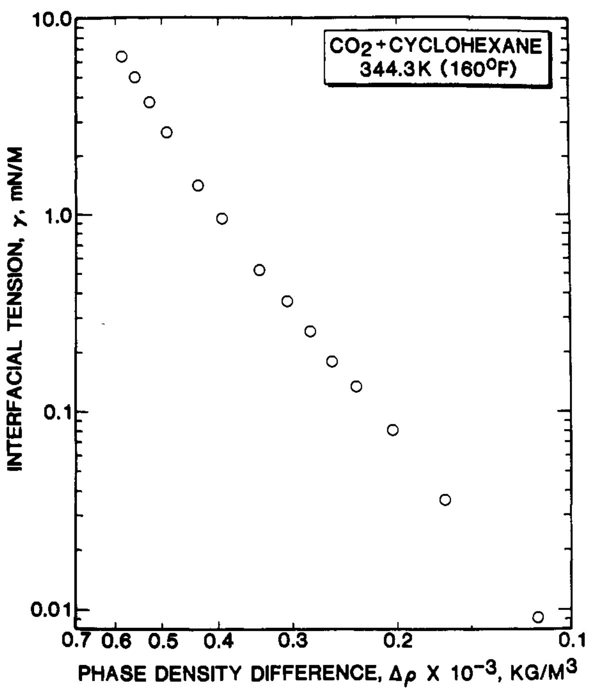

Figure 3. Interfacial tensions for CO_2 + cyclohexane at 160 °F.

meaningful comparison with the present data.

Several previous studies have been made of the phase equilibria for CO_2 + benzene (*8–10*), but none were at 160 °F. The data of Kay and Kreglewski (*10*) have been interpolated to yield values of the critical pressure and composition at 160 °F. Their critical pressure is in extremely good agreement with the present results and the critical composition is in adequate agreement (Table III).

The critical point properties in the present work were determined by methods described previously (*2*), using scaling-law relations given by

$$\Delta\rho = A_1[(P_c - P)/P_c]^{\beta} \qquad (1)$$

and

$$\gamma/\Delta\rho = A_2[(P_c - P)/P_c]^{2\nu-\beta} \qquad (2)$$

(Note: the pendant drop measurements of IFT actually give values of $\gamma/\Delta\rho$ rather than γ directly.) All data at pressures within 10% of the critical pressure were analyzed simultaneously in terms of the above two equations. Weighted regressions were performed for each system studied to determine simultaneously A_1, A_2, P_c, β, and ν. Experimental uncertainties were assigned to each measured variable as follows:

$$\epsilon_\gamma = 0.04\gamma^{0.8}\text{, mN/m} \qquad (3)$$

$$\epsilon_\rho = 0.0005 \text{ g/cm}^3 \qquad (4)$$

$$\epsilon_p = 2 \text{ psi} \qquad (5)$$

These uncertainties were used to evaluate weighting factors used in the regressions. The resultant values of P_c are shown in Tables II and III. Values determined for β, ν were 0.338, 0.632 and 0.354, 0.653 for the cyclohexane and benzene systems, respectively. These are in adequate agreement with the values of 0.355 ± 0.01 and 0.63 ± 0.02 previously reported for these scaling-law variables (*11*) from analysis of data on pure substance properties. For all data points, the fits to the equations were within the expected maximum uncertainties (estimated from the experimental uncertainties given above). Values of the critical-point densities were determined from "rectilinear diameter" plots of $(\rho^V + \rho^L)/2$ vs. $(P_c - P)$ and critical compositions from plots of $(x + y)/2$ vs. $(P_c - P)$.

In Table II, one point is denoted as "suspect" since the scaling-law analysis predicts a critical pressure very near the pressure for this two-phase data point. Measurements near the critical pressure are quite difficult; the rates of change of density and composition with pressure become infinite. Thus, although the indicated datum is presented in the table, it appears to be inconsistent with the data at lower pressures.

Conclusion

Data are presented for phase compositions, phase densities, and IFTs at 160 °F for the CO_2 + cyclohexane and CO_2 + benzene systems. The accuracy of the results appears to be comparable to our previously reported data on CO_2 + *n*-butane and CO_2 + *n*-decane. The data presented here represent measurements not previously available in the literature.

Glossary

A_1, A_2	parameters in eq 1 and 2
P	pressure
P_c	critical pressure
x	liquid-phase mole fraction
y	vapor-phase mole fraction

Greek Letters

β, ν	scaling-law parameters (critical indices)
γ	interfacial tension
ϵ_p	uncertainty in measured pressure
ϵ_γ	uncertainty in measured interfacial tension
ϵ_ρ	uncertainty in measured density
ρ^L	liquid-phase density
ρ^V	vapor-phase density
$\Delta\rho$	liquid-phase density minus vapor-phase density

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