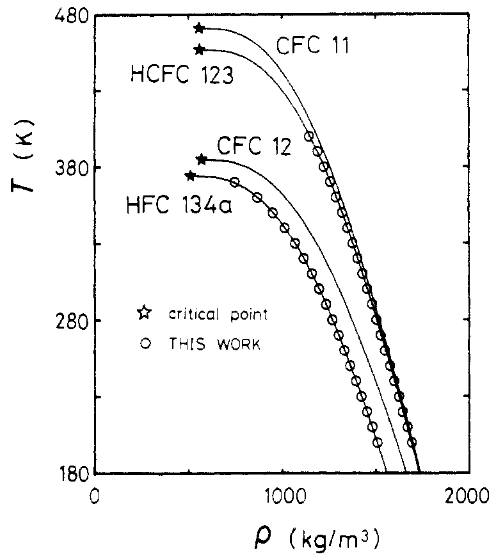

**Figure 5.** Comparison of saturated liquid densities of HCFC 123, HFC 134a, CFC 11, and CFC 12.

The present saturated liquid densities and present correlations for HCFC 123 and HFC 134a are compared with Okada's correlations (*1*) for CFC 11 and CFC 12 in Figure 5. Saturated liquid density of HCFC 123 differs by around 41 kg/m$^3$ (3.6%) from that of CFC 11 at 400 K and is closer to that of CFC 11 at lower temperatures, e.g., 4.4 kg/m$^3$ (0.3%) at 200 K. Saturated liquid density of HFC 134a is smaller than that of CFC 12 by about 100 kg/m$^3$ except in the critical region.

### Acknowledgment

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# Equilibrium Phase Compositions, Phase Densities, and Interfacial Tensions for $CO_2$ + Hydrocarbon Systems. 6. $CO_2$ + *n*-Butane + *n*-Decane

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**Experimental vapor-liquid equilibrium phase compositions, phase densities, and interfacial tensions are presented for the ternary system $CO_2$ + *n*-butane + *n*-decane at 160 °F. Measurements were made on a mixture of constant overall molar composition of 90.2% $CO_2$, 5.9% *n*-$C_4$, 3.9% *n*-$C_{10}$ at pressures from 1310 psia to a near-critical dew point state at 1675 psia. Additional data were obtained at a constant pressure of 1600 psia. The measured phase compositions are in agreement with the data of Metcalfe and Yarborough. The phase densities and interfacial tensions represent data not previously available in the literature.**

## Introduction

This work is a part of our continuing studies (*1*-*3*) of phase behavior and interfacial tension (IFT) in mixtures of $CO_2$ with a series of hydrocarbon solvents, including pure and mixed hydrocarbons and reservoir oils. The present study of the ternary system formed by $CO_2$, *n*-butane, and *n*-decane complements our earlier work on the binary systems $CO_2$ + *n*-butane (*1*) and $CO_2$ + *n*-decane (*2*).

The data from our studies provide a basis for developing/testing models for the prediction of phase behavior and IFT in these systems. The ternary data from this work provide an opportunity to test the ability of models, containing parameters optimized to describe binary data, to describe mixtures containing a larger number of components. As such, these tests form a logical bridge between binary systems and real-oil mixtures.

## Experimental Method

The experimental facility and procedures have been described in detail previously (*1*). Procedures employed in the present study were identical with those used in our $CO_2$ + *n*-decane (*2*) studies. The only difference in operating procedures involved the technique for charging materials to the apparatus, as described below.

Our primary objective was to study the effect of pressure on the phase behavior at constant temperature and, in particular, to include the near-critical region where IFT approaches zero. (This is of particular interest in enhanced oil recovery applica-

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**Table I. Phase Equilibria and Interfacial Tensions for a 90.2%/5.9%/3.9% Carbon Dioxide/n-Butane/n-Decane Mixture at 344.3 K (160 °F)**[a]

| pressure | | phase compositions, mole fraction | | | | phase densities, $10^{-3}$ kg/m$^3$ | | interfacial tension, mN/m |
|---|---|---|---|---|---|---|---|---|
| | | liquid | | vapor | | | | |
| MPa | psia | $CO_2$ | $n$-$C_4$ | $CO_2$ | $n$-$C_4$ | liquid | vapor | |
| 9.03 | 1310 | 0.637 | 0.157 | 0.948 | 0.029 | 0.6822 | 0.2348 | |
| 9.31 | 1351 | 0.643 | 0.150 | 0.949 | 0.032 | 0.6812 | 0.2498 | 2.43 |
| 9.65 | 1400 | 0.671 | 0.139 | 0.949 | 0.031 | 0.6793 | 0.2686 | 1.77 |
| 10.00 | 1451 | 0.704 | 0.129 | 0.948 | 0.034 | 0.6763 | 0.2887 | 1.34 |
| 10.35 | 1501 | 0.732 | 0.116 | 0.945 | 0.036 | 0.6717 | 0.3137 | 0.94 |
| 10.51 | 1524 | 0.744 | 0.114 | 0.943 | 0.038 | 0.6661 | 0.3269 | 0.76 |
| 10.71 | 1553 | 0.767 | 0.106 | 0.942 | 0.039 | 0.6611 | 0.3473 | 0.545 |
| 10.89 | 1580 | 0.802 | 0.098 | 0.941 | 0.039 | 0.6556 | 0.3667 | 0.405 |
| 11.04 | 1601 | 0.809 | 0.093 | 0.938 | 0.042 | 0.6483 | 0.3845 | 0.295 |
| 11.17 | 1621 | 0.826 | 0.087 | 0.934 | 0.044 | 0.6388 | 0.4046 | 0.200 |
| 11.30 | 1640 | 0.838 | 0.082 | 0.932 | 0.045 | 0.6276 | 0.4283 | 0.115 |
| 11.38 | 1651 | 0.852 | 0.078 | 0.927 | 0.048 | 0.6181 | 0.4454 | 0.064 |
| 11.45 | 1661 | 0.861 | 0.075 | 0.919 | 0.051 | 0.6070 | 0.4638 | 0.033 |
| 11.51 | 1670 | 0.874 | 0.070 | 0.911 | 0.054 | 0.5890 | 0.4915 | |
| 11.57 | 1678* | 0.902 | 0.058 | 0.903 | 0.058 | 0.5253 | 0.5213 | |

[a] Asterisk marks suspect data point.

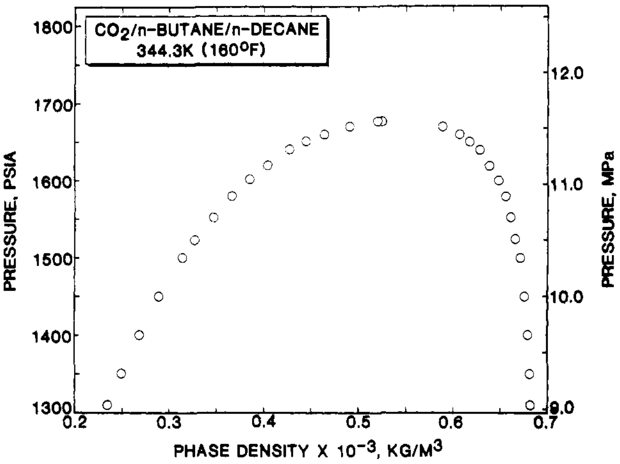

**Figure 1.** Phase densities for $CO_2$/$n$-butane/$n$-decane at 160 °F.

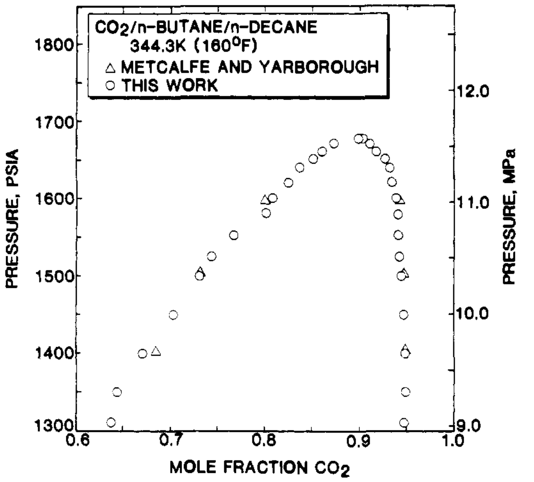

**Figure 2.** Comparison of $CO_2$ phase compositions at 160 °F.

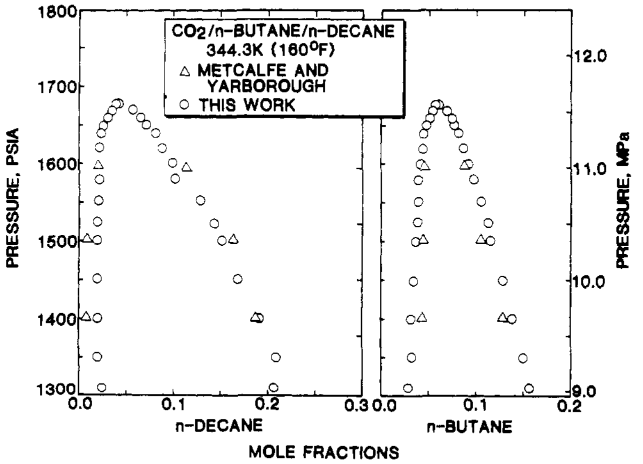

**Figure 3.** Comparisons of $n$-decane and $n$-butane phase compositions at 160 °F.

tions, since improved efficiency of oil displacement by $CO_2$ occurs when the IFT becomes low.) In our previous binary studies, the $CO_2$ and hydrocarbon were injected individually into the test cell. No record of the overall mixture composition in the apparatus was needed since, for binary mixtures, the temperature and pressure fix all properties of the equilibrium phases. For ternary and higher order mixtures, the phase properties depend on the overall mixture composition in addition to temperature and pressure. Thus, an alternate charging procedure was employed.

We chose to study a single overall composition such that the system would pass through the estimated critical point as pressure was increased. A mixture of the estimated critical composition at 160 °F was prepared by injecting known amounts of the pure components from a calibrated volumetric pump (Ruska Instrument Corp., Model 2250-803) into a variable-volume rodded transfer cell (Temco, Inc., Model CR-25-100). This mixture was maintained in a single-phase liquid state in the transfer cell at room temperature and was then charged to the experimental apparatus. The pressure in the apparatus (at the operating temperature of 160 °F) was increased in incremental steps by injecting additional amounts of material from the transfer cell. Thus, the measurements were taken on a mixture of constant overall composition in the apparatus.

## Experimental Results

Measurements of equilibrium phase densities, phase compositions, and interfacial tensions were performed at 160 °F for a mixture having an overall molar composition of 90.2% $CO_2$, 5.9% $n$-$C_4$, 3.9% $n$-$C_{10}$. The measurements cover the range from approximately 1300 psia up to the pressure at which the mixture reached a single-phase condition, and the results appear in Table I and Figures 1–4.

The mixture clearly proceeded to a dew point condition as the pressure was increased (the phase interface dropped to the bottom of the equilibrium cell); however, this dew point was *very* near the critical point of the mixture. Figures 1–3 illustrate this fact by showing the near equality of the equilibrium liquid- and

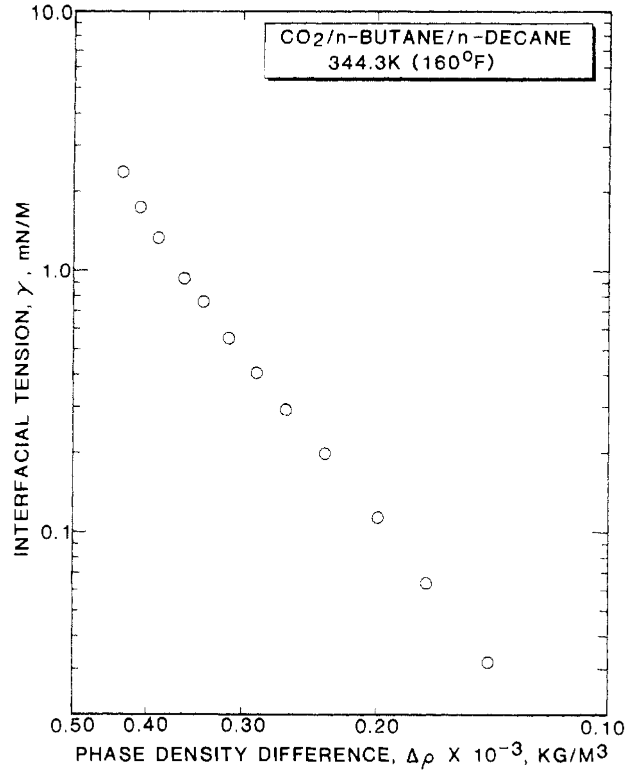

**Figure 4.** Interfacial tensions for $CO_2$/$n$-butane/$n$-decane at 160 °F.

vapor-phase densities (and compositions) at the highest pressure at which the two phases coexisted.

Figure 1 illustrates the phase densities; no previous studies are available for comparisons with these density measurements. Figures 2 and 3 show the phase compositions. Also shown are the data of Metcalfe and Yarborough (*4*) on a very similar mixture (90.4% $CO_2$, 5.9% $n$-$C_4$, 3.7% $n$-$C_{10}$). The $CO_2$ compositions from the two studies are in good agreement (Figure 2). Vapor-phase concentrations from our work are generally 0.01 mole fraction higher in $n$-decane and liquid concentrations are 0.01 lower (Figure 3). Results for $n$-butane also differ by approximately 0.01 mole fraction in the opposite direction from the $n$-decane measurements. These disagreements (0.01 mole fraction) with the data of Metcalfe and Yarborough are only slightly outside the combined experimental uncertainties in the two works, which we estimate to be approximately 0.006.

The IFT data from the present work are shown in Figure 4. No literature data are available for this system. The data are shown as a function of the difference in the equilibrium phase densities. This log–log method of presenting the data conveniently expands the low-IFT region; in addition, "scaling laws" require that this relationship becomes linear (on a log–log scale) at low IFT values and that the slope should be a specific, universal value. (This is discussed further below.)

On the basis of our previous experience, we estimate the following values for the expected experimental uncertainties, $\epsilon$, in the measured variables for the present work:

$$\epsilon_{(\gamma/\Delta\rho)} = 0.04\gamma^{0.8} \tag{1}$$

where $\gamma$ is in mN/m and $\Delta\rho$ is in g/cm$^3$.

$$\epsilon_{\rho} = 0.001 \text{ g/cm}^3 \tag{2}$$

$$\epsilon_{P} = 2 \text{ psia} \tag{3}$$

$$\epsilon_x = \epsilon_y = 0.003 \text{ (mole fraction)} \tag{4}$$

Although the present system did not pass exactly through the critical point, the saturation (dew point) condition is so near a critical point that we have estimated the "critical point properties" of the system. These values were determined as follows. Scaling law analysis suggests that

**Table II. Phase Equilibria Compositions (Mole Fraction) for Carbon Dioxide/$n$-Butane/$n$-Decane at 344.3 K (160 °F) and 1600 psia**

| liquid | | vapor | |
|---|---|---|---|
| $CO_2$ | $n$-butane | $CO_2$ | $n$-butane |
| 0.809 | 0.093 | 0.938 | 0.042 |
| 0.803 | 0.093 | 0.936 | 0.043 |
| 0.807 | 0.092 | 0.941 | 0.040 |
| 0.800 | 0.079 | 0.954 | 0.032 |
| 0.784 | 0.073 | 0.961 | 0.028 |
| 0.790 | 0.068 | 0.964 | 0.026 |
| 0.769 | 0.062 | 0.967 | 0.023 |
| 0.771 | 0.058 | 0.970 | 0.021 |
| 0.777 | 0.053 | 0.971 | 0.020 |

$$\Delta\rho = A_1[(P_c - P)/P_c]^{\beta} \tag{5}$$

$$\gamma/\Delta\rho = A_2[(P_c - P)/P_c]^{2\nu-\beta} \tag{6}$$

(Note: Pendant drop measurements of IFT actually give values of $\gamma/\Delta\rho$ rather than $\gamma$ directly.) Data at pressures within 10% of the "critical" pressure were analyzed simultaneously in terms of the above two equations. Weighted regressions were performed to determine simultaneously $A_1$, $A_2$, $P_c$, $\beta$, and $\nu$. The experimental uncertainties given in eqs 1–3 were used to evaluate weighting factors for use in the regressions. The resultant value of $P_c$ is 1674 psia. The values determined for $\beta$ and $\nu$, 0.359 and 0.654, respectively, are in adequate agreement with reported experimental values of 0.36 ± 0.01 and 0.63 ± 0.02 for these scaling law exponents (*5*). For all data points, the fit to the equations was within the expected maximum uncertainty (estimated from the experimental uncertainties given above). The value of the critical point density, determined from a "rectilinear diameter" plot of $(\rho^V + \rho^L)/2$ vs $P_c - P$, is 0.540 g/cm$^3$.

In Table I, the data point at the highest pressure (1678 psia) is denoted as "suspect" since the scaling law analysis predicts a critical pressure below the pressure for that two-phase data point. Measurements very near the critical pressure were quite difficult, since the rates of change of the equilibrium phase densities and compositions with respect to pressure become infinite. Thus, although the indicated data point is presented in the table, it appears to be inconsistent with the data at lower pressures.

In the course of the present work, selected additional phase composition measurements were made on the ternary system at 160 °F and 1600 psia. The data were taken by varying the overall mixture composition in such a way that the system pressure remained at 1600 psia. Results appear in Table II and Figure 5. These measurements were done to permit further comparisons with the data of Metcalfe and Yarborough, as shown in Figure 5. (Note the expanded scale of this figure.) In general, agreement is adequate; the size of the symbols in the figure corresponds to the expected experimental uncertainty in the data points.

## Correlation

The data reported here, in addition to our $CO_2$ + $n$-butane and $CO_2$ + $n$-decane data, have been used to test the Weinaug–Katz (W–K) equation (*6*) for prediction of mixture IFT. The W–K equation, the most widely used technique for IFT predictions, may be written in the general form

$$\gamma = [\sum_{i=1}^{N} P_i(\rho^L x_i - \rho^V y_i)]^k \tag{7}$$

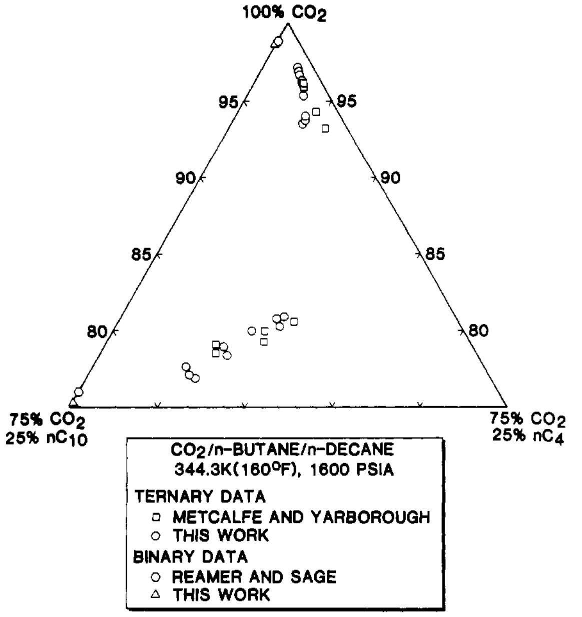

**Figure 5.** Comparison of phase compositions for $CO_2$/*n*-butane/*n*-decane at 160 °F and 1600 psia.

where $P_i = \gamma_i^{(1/k)}/\Delta\rho_i$. The original W-K model sets $k = 4$; however, comparing the pure substance form of eq 7 with near-critical power law behavior

$$\gamma = A_3 \Delta\rho^{2\nu/\beta} \tag{8}$$

suggests that (at least in the region of the critical point) $k$ should be of the range from 3.55 to 3.89 (*5*, *7*).

In our previous evaluation of the available data for mixtures of $CO_2$ (and ethane) with hydrocarbons (*8*), we found optimum values of the parachors, $P_i$, for $CO_2$, *n*-butane, and *n*-decane to be 73.5, 203.4, and 446.2, respectively, with $k = 3.6$. With these values, the W-K model describes our data with average absolute percent deviations of 3.9%, 6.4%, and 9.9% for the $CO_2$ + *n*-$C_4$, $CO_2$ + *n*-$C_{10}$, and $CO_2$ + *n*-$C_4$ + *n*-$C_{10}$ systems, respectively. These results, illustrated in Figure 6, suggest that the simple W-K relation, with a suitably modified exponent, $k$, can provide adequate representation of IFT for many applications. However, the user must bear in mind that experimental phase compositions and densities were employed in the above evaluations. In applications where these input variables must be estimated (e.g., from an equation of state), larger errors in predicted IFT are likely.

## Conclusion

Data are presented at 160 °F for phase compositions, phase densities, and interfacial tensions for the ternary system $CO_2$ + *n*-butane + *n*-decane. Accuracy of the data is comparable to our previous measurements. The phase density and IFT behaviors have not been measured previously, and the phase compositions agree with earlier measurements of Metcalfe and Yarborough. At pressures within 10% of the critical pressure, the data obey asymptotic forms of scaling relations (eqs 5 and 6). The Weinaug-Katz equation is capable of representing the IFT data with an average absolute percentage error of 10% when an exponent of 3.6 is used in the equation.

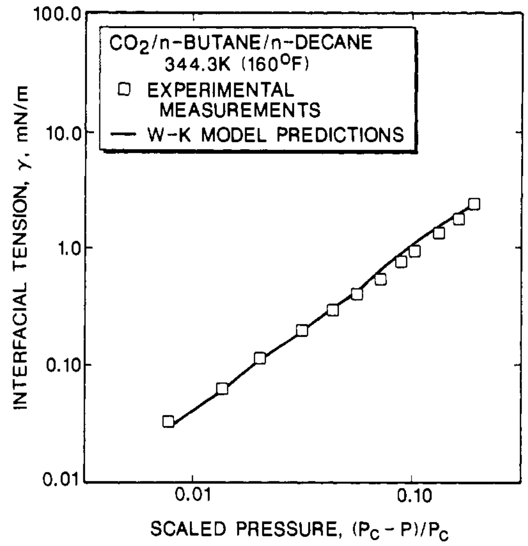

**Figure 6.** Weinaug-Katz model predictions of interfacial tensions of $CO_2$/*n*-butane/*n*-decane at 160 °F.

## Glossary

| | |
|---|---|
| $A_1$, $A_2$, $A_3$ | parameters in eqs 5, 6, and 8 |
| $P$ | pressure |
| $P_c$ | critical pressure |
| $P_i$ | parachor of component *i* |
| $N$ | number of components in mixture |
| $x$ | liquid-phase mole fraction |
| $y$ | vapor-phase mole fraction |
| $\beta$, $\nu$ | scaling law parameters (critical indices) |
| $\gamma$ | interfacial tension |
| $\epsilon_P$ | uncertainty in measured pressure |
| $\epsilon_\rho$ | uncertainty in measured density |
| $\epsilon_x$, $\epsilon_y$ | uncertainties in measured compositions |
| $\epsilon_\gamma$ | uncertainty in measured interfacial tension |
| $\rho^L$ | liquid-phase density |
| $\rho^V$ | vapor-phase density |
| $\Delta\rho$ | liquid-phase density minus vapor-phase density, $\rho^L - \rho^V$ |

**Registry No.** $CO_2$, 124-38-9; butane, 106-97-8; decane, 124-18-5.

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