

# Vapor-Liquid Equilibrium of the Octane/Carbon Dioxide, Octane/Ethane, and Octane/Ethylene Systems

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Equilibrium phase compositions have been measured for the binary mixtures of octane plus one of three supercritical fluids: carbon dioxide, ethane, and ethylene at temperatures from 313.15 to 348.15 K over pressure ranges from the subcritical to the supercritical pressures of the solvents. Equilibrium vaporization ratios of each component were calculated on the basis of the corresponding phase compositions. The measured data were also correlated with the Soave, Patel-Teja, and Iwal-Margerum-Lu equations of state, respectively. Fair reproduction was obtained from the Patel-Teja equation.

## Introduction

It is still unsatisfactory to correlate the phase equilibrium data of the mixtures containing a supercritical component by using an equation of state. The expansion of the related experimental data is urgently needed for the model improvement. Consequently, a series of phase equilibrium measurements has been implemented in our laboratory for the binary mixtures involving a  $C_8$  solute and one of three supercritical fluids: carbon dioxide, ethane, and ethylene. This paper reports the observed results of the binary systems of octane plus the supercritical fluid at temperature ranges from 313.15 to 348.15 K and pressures up to near the critical pressures of the mixtures. Among these binary systems, King et al. (1) reported the equilibrium data of octane/carbon dioxide at 313.15 and 383.15 K. Schneider et al. (2) investigated the liquid-vapor critical curve for the same system as well. The equilibrium phase properties of the octane/ethane mixture have been observed by Rodrigues et al. (3) at temperatures ranging from 273.15 to 373.15 K and pressures up to 52.7 bar, slightly beyond the critical pressure of ethane.

## Experimental Section

The design of the semiflow apparatus in this work, basically, is similar to that reported by Lee and Chao (4). Two Monel sampling cylinders (Matheson Gas Products), 300 cm<sup>3</sup> internal volume each, are connected in series and immersed in a Neslab thermostat (model EX-251HT). The temperature of the water bath can be controlled within  $\pm 0.01$  K, and the temperature of the equilibrium system is measured with a Micro-Therm thermometer (model 1006, Hart Scientific) via a platinum RTD probe. The temperature readings were calibrated to better than  $\pm 0.04$  K.

A double-headed, constant-flow-rate fluid metering pump (model ConstaMetric 3200, LDC Analytical Inc.) is used to compress the supercritical fluids, if high pressures are required. Each head is equipped with a cooling jacket wherein aqueous ethylene glycol (about 263 K) is circulated to improve the fluid compression. A pressure transducer (model PDCR 330, 0-400 bar, Druck products) is connected to the outlet of the equilibrium cell. The readings are displayed by a digital indicator (model DPI 261, Druck products), which was calibrated to  $\pm 0.1\%$  by the manufacturer.

Table I. Phase Compositions and  $K$  Values of Octane (1) + Carbon Dioxide (2)

$T/K$	$p/\text{bar}$	$x_1$	$y_1$	$K_1$	$K_2$
313.15	15.0	0.8567	0.0053	0.006187	6.941
	30.0	0.7090	0.0040	0.005642	3.423
	45.0	0.5450	0.0044	0.008073	2.188
	58.9	0.3840	0.0047	0.01224	1.616
	65.0	0.2890	0.0048	0.01661	1.400
328.15	75.5	0.1100	0.0080	0.07273	1.115
	20.0	0.8260	0.0071	0.008596	5.706
	40.0	0.6680	0.0060	0.008982	2.994
	55.0	0.5380	0.0063	0.01171	2.151
	65.0	0.4490	0.0062	0.01381	1.804
348.15	80.0	0.2907	0.0101	0.03474	1.396
	95.0	0.1185	0.0260	0.2194	1.105
	20.0	0.8550	0.0144	0.01684	6.797
	40.0	0.7250	0.0109	0.01503	3.597
	52.6	0.6400	0.0102	0.01594	2.749
	71.0	0.5145	0.0126	0.02449	2.034
	91.0	0.3690	0.0176	0.04770	1.557
	97.0	0.3230	0.0214	0.06625	1.445
	108.0	0.2460	0.0380	0.1545	1.276
	113.5	0.1870	0.0419	0.2241	1.178

The procedures of the operation and sampling are also similar to the work of Lee and Chao (4). The solute component (octane) contained in either liquid or vapor sample is collected in a flask, which is immersed in a cold bath (263-268 K). The amount of the condensate vaporized into the liberated gas is corrected by using its vapor pressure at the collecting temperature. The minor correction of the supercritical fluids dissolved in the condensate is made according to Henry's law.

The equilibrium ratios ( $K_i = y_i/x_i$ ) of the toluene/carbon dioxide system at 352.7 K determined from our apparatus are compared with those reported by Ng and Robinson (5) as shown in Figure 1. The equilibrium ratios of both components are in agreement with the literature values within 2%.

Carbon dioxide (99.99%) was supplied by APCI, and ethane (99.0%) and ethylene (99.5%) were purchased from Matheson Gas Products. Octane and toluene supplied by Aldrich Chemical Co. has a purity of 99+%. No further purification for those chemicals was made.

## Results

The apparatus was used to measure the equilibrium compositions of octane/carbon dioxide, octane/ethane, and octane/ethylene mixtures at three different temperatures ranging from 313.15 to 348.15 K and pressures up to near the critical pressures of the mixtures. Three or four replicates were taken at each of the conditions. Reproducibility of the replications are generally better than 2%.

The equilibrium compositions and  $K$  values of the octane/carbon dioxide, octane/ethane, and octane/ethylene systems are given in Tables I, II, and III, respectively. Figures 2-4 illustrate the phase boundaries of the binary mixtures, and an enlarged scale of the vapor composition diagram is also presented for each system. It is seen that the highest measured pressure of each isotherm almost reaches its critical point, and a linear relation between the solubility of the light component and pressure exists at the low-pressure region where Henry's law is applied. In Figure 3, three additional isotherms repre-

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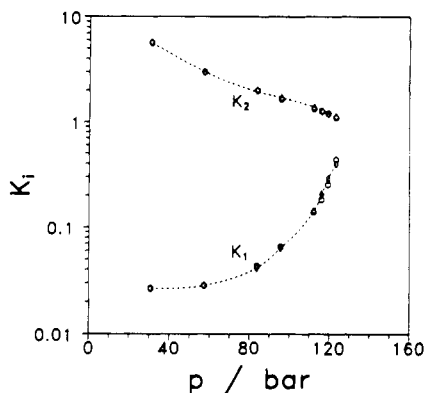


Figure 1. Equilibrium ratios for the toluene (1) + carbon dioxide (2) system: (O) 352.6 K, Ng and Robinson (S); (D) 352.7 K, this work.

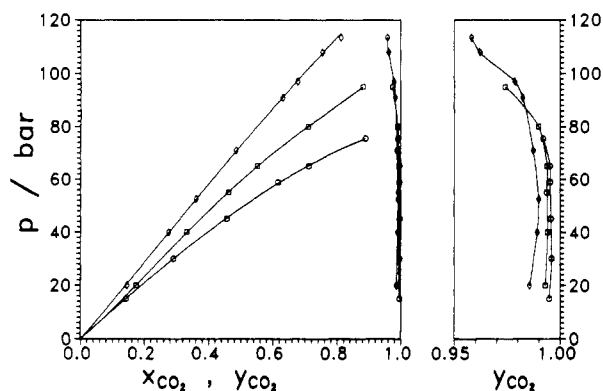


Figure 2. Phase equilibrium compositions for the octane + carbon dioxide system: (O) 313.15 K; (□) 328.15 K; (D) 348.15 K.

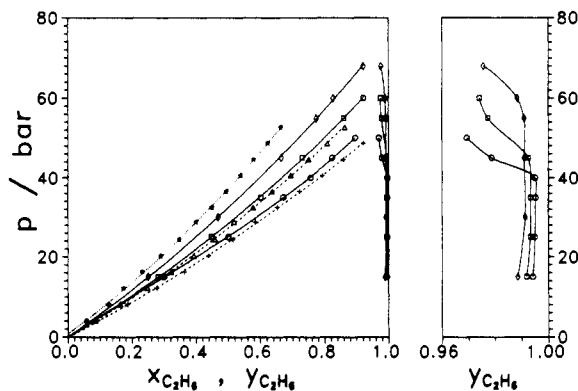


Figure 3. Phase equilibrium compositions of the octane + ethane system (O) 318.15 K; (□) 328.15 K; (D) 338.15 K, this work; (+) 313.15 K; (Δ) 323.15 K; (\*) 348.15 K, Rodrigue et al. (3).

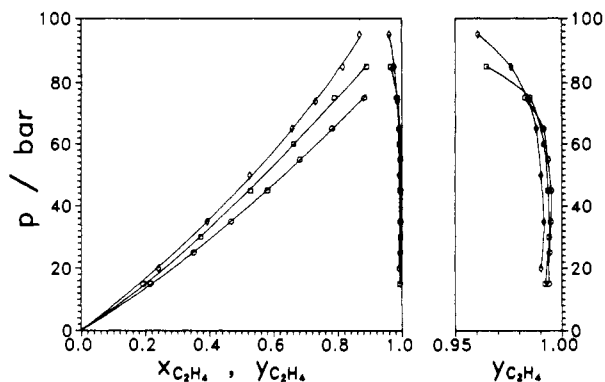


Figure 4. Phase equilibrium compositions of the octane + ethylene system (O) 318.15 K; (□) 328.15 K; (D) 338.15 K.

Table II. Phase Compositions and  $K$  Values of Octane (1) + Ethane (2)

$T/K$	$p/\text{bar}$	$x_1$	$y_1$	$K_1$	$K_2$
318.15	15.0	0.70080	0.00582	0.008305	3.323
	25.0	0.50039	0.00514	0.01027	1.991
	35.0	0.32949	0.00481	0.01460	1.484
	40.0	0.24516	0.00512	0.02088	1.318
	45.0	0.11705	0.02144	0.12110	1.189
	50.0	0.10442	0.03078	0.29480	1.082
328.15	15.0	0.71889	0.00824	0.01146	3.528
	25.0	0.55210	0.00683	0.01237	2.217
	35.0	0.39943	0.00680	0.01702	1.654
	45.0	0.27091	0.00707	0.02610	1.362
	55.0	0.14090	0.02285	0.16220	1.137
	60.0	0.07866	0.02604	0.33100	1.057
338.15	15.0	0.75068	0.01155	0.01539	3.965
	30.0	0.53264	0.00881	0.01654	2.121
	45.0	0.33616	0.00906	0.02695	1.493
	55.0	0.22703	0.00917	0.04039	1.282
	60.0	0.17374	0.01170	0.06734	1.196
	68.0	0.07888	0.02446	0.03101	1.059

Table III. Phase Compositions and  $K$  Values of Octane (1) + Ethylene (2)

$T/K$	$p/\text{bar}$	$x_1$	$y_1$	$K_1$	$K_2$
318.15	15.0	0.78374	0.00618	0.007885	4.595
	25.0	0.65078	0.00583	0.008958	2.847
	35.0	0.53205	0.00521	0.009792	2.126
	45.0	0.41965	0.00506	0.01206	1.714
	55.0	0.31933	0.00654	0.02048	1.460
	65.0	0.21900	0.00857	0.03913	1.269
328.15	15.0	0.80758	0.00785	0.009720	5.156
	30.0	0.62765	0.00607	0.009671	2.669
	45.0	0.47196	0.00650	0.01377	1.881
	60.0	0.33799	0.00836	0.02473	1.498
	75.0	0.21192	0.01497	0.07064	1.250
	85.0	0.11030	0.03558	0.3226	1.084
338.15	20.0	0.75932	0.00974	0.01283	4.114
	35.0	0.60695	0.00844	0.01391	2.523
	50.0	0.47520	0.00980	0.02062	1.887
	65.0	0.34397	0.01205	0.03503	1.506
	73.9	0.26982	0.01549	0.05741	1.348
	85.0	0.18584	0.02396	0.1289	1.199
95.0	0.13260	0.03950	0.2979	1.107	

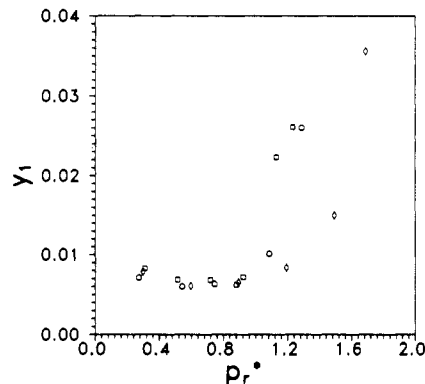


Figure 5. Variations of saturated vapor composition of octane ( $y_1$ ) with reduced pressure ( $p_r^*$ ) for octane + carbon dioxide (O), octane + ethane (□), and octane + ethylene (D) systems at 328.15 K.

sented by dashed curves are the ethane solubilities in octane at 313.15, 323.15, and 348.15 K reported by Rodrigue et al. (3). All the six isotherms follow the sequence with respect to temperature. However, it appears that the solubility differences between 323.15 and 328.15 K isotherms are rather small at pressures higher than 30 bar.

The variations of the saturated vapor composition of octane with reduced pressure in different solvents at 328.15 K are shown in Figure 5. It is indicated that the saturated molar fractions of octane are insensitive to pressure at the subcritical

Table IV. Phase Equilibrium Calculations from the Soave, Patel-Teja (PT), and Iwai-Margerum-Lu (IML) Equations of State

compd 2	Soave			PT			IML		
	$k_{a_{12}}$	$K_1$ AAD/%	$K_2$ AAD/%	$k_{a_{12}}$	$K_1$ AAD/%	$K_2$ AAD/%	$k_{a_{12}}$	$K_1$ AAD/%	$K_2$ AAD/%
CO <sub>2</sub>	0.1233	9.5	3.4	0.1188	7.8	2.0	0.1009	15.5	2.3
C <sub>2</sub> H <sub>6</sub>	0.0960	17.5	1.1	-0.0084	15.5	0.9	-0.0046	17.0	0.8
C <sub>2</sub> H <sub>4</sub>	0.0146	7.7	2.3	-0.0059	7.3	0.6	0.0068	16.2	0.9
grand av %		11.4	2.3		10.0	1.2		16.2	1.4

pressures of the solvents, i.e.,  $p_r^* (=p/p_{c,2}) < 1$ , whereas they increase remarkably as the pressures are greater than the solvents' critical pressures. Since the critical temperatures of carbon dioxide and ethane are quite close, the reduced temperatures ( $T_r^* = T/T_{c,2}$ ) of these two isotherms are almost the same, resulting in the saturated vapor compositions not being much different between these two systems over the entire pressure range. The critical temperature of ethylene, however, is substantially lower than that of carbon dioxide and of ethane, leading the vapor compositions of the ethylene-containing system to be well below those of two other mixtures as the reduced pressures are greater than unity.

#### Data Correlations

The equilibrium ratios determined in this study are correlated by the Soave (6), Patel-Teja (7) and Iwai-Margerum-Lu (8) equations of state, respectively. A quadratic mixing rule with a geometric average combining rule is used to calculate each of the mixture parameters:  $a_m$ ,  $b_m$ , and  $c_m$ , respectively. Only one adjustable binary interaction constant,  $k_{a_{12}}$ , is introduced into the combining rule for  $a_{12}$ .

$$a_m = \sum_{j=1}^2 \sum_{i=1}^2 x_i x_j a_{ij} \quad (1)$$

with

$$a_{12} = (1 - k_{a_{12}})(a_{11}a_{22})^{0.5} \quad (2)$$

where  $a_{ij}$ ,  $a_{12}$ ,  $a_{11}$ , and  $a_{22}$  are the energy parameters for  $i$ - $j$  molecule pair interaction, 1-2 molecule pair interaction, pure component 1, and pure component 2, respectively. The optimal value of  $k_{a_{12}}$  for each binary system is obtained by the minimization of the following objective function,  $\pi$ , with a modified Levenberg and Marquardt algorithm.

$$\pi = (1/2n) \sum_{k=1}^n \left( \frac{|K_1^{\text{calc}} - K_1^{\text{expt}}|}{K_1^{\text{expt}}} + \frac{|K_2^{\text{calc}} - K_2^{\text{expt}}|}{K_2^{\text{expt}}} \right) \quad (3)$$

where  $K_i^{\text{expt}} = y_i^{\text{expt}}/x_i^{\text{expt}}$  and  $K_i^{\text{calc}}$  denotes the calculated  $K$  value for the component  $i$ ; that is

$$(\Phi_i^1/\Phi_i^v)^{\text{calc}} = (y_i/x_i)^{\text{calc}} = K_i^{\text{calc}} \quad (4)$$

where  $\Phi_i^1$  and  $\Phi_i^v$  are the fugacity coefficient of component  $i$  for the liquid phase and vapor phase, respectively. The values can be calculated from the equation of state with a given  $k_{a_{12}}$ . If  $K_i^{\text{calc}}$  equals  $K_i^{\text{expt}}$ , the model exactly reproduces the equilibrium ratio. Therefore, the value of the objective function defined in eq 4 is a measure of the quality of the model (9). However, it should be noted that the weighting of the objective function from  $K_1$  is greater than that from  $K_2$  because the  $K$  values of the heavy component (1) are always lower than those of the light component (2). The results of data reduction are tabulated in Table IV, indicating that the Patel-Teja equation gives the best representation. Among these three binary systems, the average absolute deviation (AAD) of the equilibrium ratios of the octane component for the ethane-containing system is relatively high (15.5%). A worse result, the AAD of  $K_1$

as high as 39.8%, is also obtained when the literature data (3) of the same system at 313.15, 323.15, and 348.15 K over the pressure ranging from 16.2 to 48.6 bar are correlated by the Patel-Teja equation of state. For such a system, not much improvement was made as we used either temperature-dependent  $k_{a_{12}}$  or the best fit equation parameters ( $\zeta_c$  and  $F$  for the Patel-Teja equation) of the octane component. To improve the phase equilibrium calculation, the Patel-Teja equation with a linear density-dependent mixing rule is under investigation.

#### Glossary

$a, b, c$	parameters in the equation of state
$F$	parameter in the Patel-Teja equation
$k_{a_{12}}$	binary interaction constant for 1-2 molecule pair
$K_{12}$	equilibrium vaporization ratio
$n$	number of data points
$p$	pressure
$p_r^*$	reduced pressure ( $=p/p_{c,2}$ )
$T$	temperature
$T_r^*$	reduced temperature ( $=T/T_{c,2}$ )
$x$	mole fraction in liquid phase
$y$	mole fraction in vapor phase
$\zeta_c$	hypothetical critical compressibility factor
$\pi$	objective function
$\Phi_i$	fugacity coefficient for component $i$

#### Superscripts

calc	calculated value
expt	experimental data
l	liquid phase
v	vapor phase

#### Subscripts

1	component 1
12	1-2 molecule pair
2	component 2
$i$	component $i$
$ij$	$i$ - $j$ molecule pair
m	mixture

Registry No. Octane, 111-65-9; carbon dioxide, 124-38-9; ethane, 74-84-0; ethene, 74-85-1.

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