As iodine compounds have a peculiar behavior, aqueous HI solutions may be ordered near the minimum density points.

In hydrogen energy recycle processes it is convenient to flow aqueous HI solutions of minimum viscosities in pipes, as the pressure drop of the solution through the pipes is minimum.

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Three-Phase Liquid–Liquid–Vapor Equilibria Behavior of Certain Binary CO_2–*n*-Paraffin Systems

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The three-phase liquid–liquid–vapor loci of four binary CO_2–*n*-paraffin systems (*n*-dodecane, *n*-tridecane, *n*-tetradecane, *n*-pentadecane) are studied, and temperature, pressure, and molar volumes and compositions of both liquid phases are reported. It is within this group of *n*-paraffins that the nature of the upper critical end point for the CO_2-containing binary systems changes from a UCST (L—L-V) to a K point (L-L—V) with increasing carbon number. These four loci are compared with earlier obtained loci on CO_2–*n*-decane and CO_2–*n*-eicosane.

Introduction

There is an increasing interest in CO_2–hydrocarbon phase equilibria data relevant to the process of using CO_2 injection for enhanced oil recovery. Such data are useful for determining interaction parameters in equations of state purporting to be applicable to describing the phase equilibria in such multicomponent systems. These equations of state would be used to describe three-phase L_1–L_2–V phase equilibria as well as two-phase L–V and L_1–L_2 phase equilibria (*1*).

Schneider (*2*) has reported that the binary L_1–L_2–V loci of the CO_2–*n*-paraffin systems undergo a transition in phase behavior as one increases the carbon number. Specifically, the CO_2–*n*-tridecane locus terminates at the upper end (higher *P* and *T* end) with a UCST (L_1—L_2–V) while the CO_2–*n*-hexadecane locus terminates with a K point (L_1–L_2—V). This observation is consistent with our detailed studies of the binary systems CO_2–*n*-decane (*3*) and CO_2–*n*-eicosane (*4*), the former exhibiting a UCST and the latter a K point as the upper termination point to its L_1–L_2–V locus.

In this paper, we present detailed studies of the L_1–L_2–V loci of the binary systems CO_2 with *n*-dodecane, *n*-tridecane, *n*-tetradecane, and *n*-pentadecane, respectively. Knowledge of these systems in the vicinity of the above-mentioned transformation in L_1–L_2–V loci will be useful to testing correlations and obtaining interaction parameters for L_1–L_2–V phase equilibria calculations. In particular, a strong case could be made for a correlation which not only predicts L_1–L_2–V phase equilibria for these binary systems but also correctly signals the change in L_1–L_2–V loci with increasing carbon number at the correct place, namely (as will be shown), between the systems CO_2–*n*-tridecane and CO_2–*n*-tetradecane.

Experimental Section

A detailed description of the experimental equipment and procedure is given elsewhere (*4*, *5*). Briefly, a known amount of *n*-paraffin was placed in a 10-mL glass equilibrium cell. During experimental runs, measured amounts of CO_2 gas were added to the thermostated equilibrium cell from a high-pressure bomb, through the use of a positive displacement mercury pump. By a mass balance the moles of CO_2 in a liquid phase can be determined (the vapor phase is assumed to be pure CO_2 due to the low volatility of these paraffins at the temperatures of interest). In studying a L_1–L_2–V system, the moles of CO_2 in an *individual* liquid phase were determined by making a run in which the *other* liquid phase was present in a trace (but visible) amount. Thus two runs were required to obtain the properties of both L_1 and L_2. Procedures for determining the termination points of the L_1–L_2–V loci (see Table V) are routine and are detailed elsewhere (*4*).

Temperature was measured with a Pt-resistance thermometer to an estimated accuracy of ±0.02 K for the L_1–L_2–V data. Pressure was measured with Bourdon tube gauges, which were frequently calibrated against an accurate dead-weight gauge, to an estimated accuracy of ±0.07 bar. The viewable glass equilibrium cell was volumetrically marked and calibrated and gave volumetric readings to an accuracy of ±0.02 mL.

Materials

The *n*-paraffins were purchased from the Humphrey-Wilkinson Co. at a stated purity of 99%. Melting point depression determinations indicated impurity levels of 0.47% (*n*-dodecane), 2.02% (*n*-tridecane), 1.12% (*n*-tetradecane), and 0.34% (*n*-pentadecane) based on literature values (*6*) of the melting points. The *n*-paraffins were used without further purification.

The CO_2 (mol wt = 44.01) used in this study was obtained from the Matheson Co. as "Coleman Grade" material with a stated minimum purity of 99.99%. Oxygen, nitrogen, carbon monoxide, and hydrogen were the major impurities.

The CO_2 was prepared for use by flashing it from the cylinder at room temperature to the 2000-cm^3 storage reservoir maintained at 0 °C. When this is done, the resulting liquefaction of the CO_2 makes it free from impurities, the impurities remaining

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Table I. Smoothed Values of Pressure, Compositions, and Liquid Molar Volumes as a Function of Temperature for Carbon Dioxide-*n*-Dodecane

temp, K	press., bar	CO$_2$ mole fraction L_1	L_2	molar vol, mL/(g-mol) v_{L_1}	v_{L_2}	comments
254.28	20.06	0.657	0.9749	104.7	47.5	Q(S_1-L_1-L_2-V)
256.0	21.1	0.678	0.9722	101.8	48.3	L_1-L_2-V
258.0	22.3	0.702	0.9680	98.2	49.2	L_1-L_2-V
260.0	23.6	0.722	0.9627	94.2	50.3	L_1-L_2-V
262.0	25.0	0.743	0.9570	90.0	51.8	L_1-L_2-V
264.0	26.4	0.761	0.9480	85.3	53.9	L_1-L_2-V
266.0	27.8	0.812	0.9340	79.1	57.3	L_1-L_2-V
267.31	28.82	0.870	0.870	68.3	68.3	UCST(L_1=L_2-V)
SD	0.06	0.001	0.0006	0.3	0.2	

Table II. Smoothed Values of Pressure, Compositions, and Liquid Molar Volumes as a Function of Temperature for Carbon Dioxide-*n*-Tridecane

temp, K	press., bar	CO$_2$ mole fraction L_1	L_2	molar vol, mL/(g-mol) v_{L_1}	v_{L_2}	comments
255.16	20.76	0.611	0.9842	117.2	46.2	Q(S_1-L_1-L_2-V)
256.0	21.3	0.626	0.9838	115.5	46.6	L_1-L_2-V
258.0	22.6	0.650	0.9815	112.0	47.5	L_1-L_2-V
260.0	23.9	0.670	0.9795	108.7	48.4	L_1-L_2-V
262.0	25.3	0.687	0.9770	105.7	49.3	L_1-L_2-V
264.0	26.7	0.703	0.9750	102.8	50.2	L_1-L_2-V
266.0	28.2	0.720	0.9722	99.8	51.1	L_1-L_2-V
268.0	29.7	0.737	0.9692	96.7	52.2	L_1-L_2-V
270.0	31.3	0.755	0.9655	93.5	53.2	L_1-L_2-V
272.0	33.0	0.773	0.9617	90.2	54.4	L_1-L_2-V
274.0	34.8	0.793	0.9570	87.0	55.8	L_1-L_2-V
276.0	36.6	0.813	0.9490	83.5	57.8	L_1-L_2-V
273.0	38.4	0.837	0.9340	79.2	61.0	L_1-L_2-V
278.95	39.33	0.860	0.860	74.4	74.4	UCST(L=L_2-V)
SD	0.08	0.001	0.0002	0.5	0.2	

Table III. Smoothed Values of Pressure, Compositions, and Liquid Molar Volumes as a Function of Temperature for Carbon Dioxide-*n*-Tetradecane

temp, K	press., bar	CO$_2$ mole fraction L_1	L_2	molar vol, mL/(g-mol) v_{L_1}	v_{L_2}	comments
269.10	30.82	0.703	0.9821	105.9	50.6	Q(S_1-L_1-L_2-V)
270.0	31.1	0.707	0.9815	104.8	50.9	L_1-L_2-V
275.0	35.5	0.738	0.9747	96.8	53.2	L_1-L_2-V
280.0	40.8	0.768	0.9695	93.8	55.4	L_1-L_2-V
285.0	46.1	0.796	0.9655	89.8	57.6	L_1-L_2-V
290.0	51.8	0.816	0.9627	87.2	59.5	L_1-L_2-V
295.0	58.0	0.826	0.9627	86.1	61.3	L_1-L_2-V
300.0	64.9	0.832	0.9678	86.0	62.8	L_1-L_2-V
305.0	72.4	0.837	0.9760	85.1	65.1	L_1-L_2-V
310.0	80.6	0.840	0.9862	81.4	69.3	L_1-L_2-V
311.15	82.60	0.840		77.3		K(L_1-L_2=V)
SD	0.20	0.002	0.0009	0.7	0.4	

Table IV. Smoothed Values of Pressure, Compositions, and Liquid Molar Volumes as a Function of Temperature for Carbon Dioxide-*n*-Pentadecane

temp, K	press., bar	CO$_2$ mole fraction L_1	L_2	molar vol, mL/(g-mol) v_{L_1}	v_{L_2}	comments
270.40	31.94	0.680	0.9883	117.8	49.3	Q(S_1-L_1-L_2-V)
275.0	36.0	0.704	0.9862	112.8	50.4	L_1-L_2-V
280.0	40.9	0.727	0.9840	108.4	51.8	L_1-L_2-V
285.0	46.2	0.749	0.9816	104.8	53.4	L_1-L_2-V
290.0	52.1	0.764	0.9807	101.8	55.3	L_1-L_2-V
295.0	58.5	0.775	0.9812	99.9	57.6	L_1-L_2-V
300.0	65.5	0.782	0.9840	98.7	60.3	L_1-L_2-V
305.0	73.0	0.786	0.9893	98.2	64.6	L_1-L_2-V
309.41	80.22	0.788		98.1		K(L_1-L_2-V)
SD	0.20	0.001	0.0003	0.5	0.6	

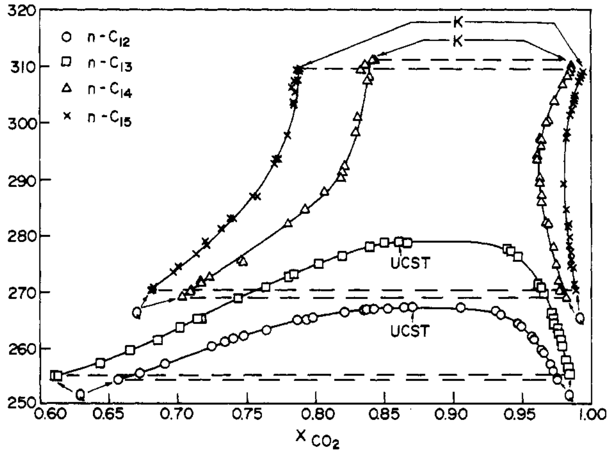

Figure 1. Temperature vs. mole fraction of CO$_2$ data for the two liquid phases in the four binary CO$_2$–*n*-paraffin systems. The smoothed curves correspond to Tables I–IV, with the CO$_2$-rich portions of the curves corresponding to the L_2 phases.

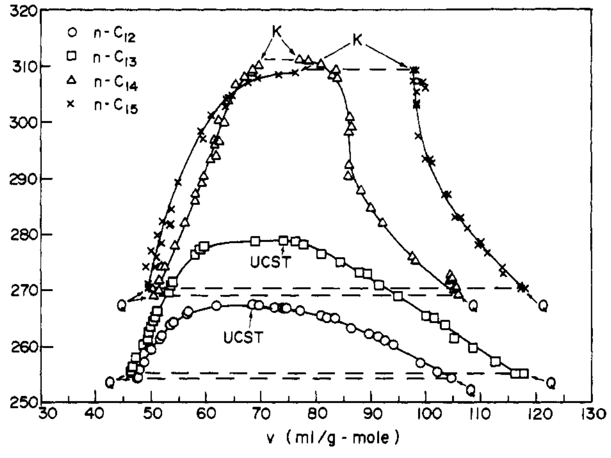

Figure 2. Temperature vs. molar volume data for the two liquid phases in the four binary CO$_2$–*n*-paraffin systems. The smoothed curves correspond to Tables I–IV, with the smaller molar volume portions of the curves corresponding to the L_2 phases.

in the vapor space. Subsequent venting of the vapor phase in the reservoir then removes these impurities.

The Kuenen criterion of purity (the difference between the bubble point and the dew point pressure divided by the critical pressure) was 0.0056 at 298.16 K. The properties vapor pressure, sublimation pressure, and critical and triple point were within 0.3 bar and 0.1 K of the literature values (*7*).

Results

Table I–IV present smoothed L_1 and L_2 data on the binary systems CO$_2$–*n*-dodecane, CO$_2$–*n*-tridecane, CO$_2$–*n*-tetradecane, and CO$_2$–*n*-pentadecane. Figures 1 and 2 give composition and molar volume as a function of temperature for the L_1 and L_2 phases, showing both raw and smoothed data. For the system CO$_2$–*n*-dodecane, 18 L_1 and 13 L_2 data points were taken; for the system CO$_2$–*n*-tridecane, 18 L_1 and 17 L_2 data points were taken; for the system CO$_2$–*n*-tetradecane, 22 L_1 and 26 L_2 data points were taken; for the system CO$_2$–*n*-pentadecane, 27 L_1 and 25 L_2 data points were taken. Tables I–IV give standard deviations for the data based on a comparison of the smoothed data with the raw data. The smoothed data curves were arrived at visually.

Table V is a listing of the end points of the L_1–L_2–V locus of each of the four systems studied as well as for the CO$_2$–*n*-

Table V. L-L-V Locus End Points for the Four Binary Systems Studied and Also for the Binary Systems CO_2-*n*-Decane (*4*) and CO_2-*n*-Eicosane (3)

system	type	temp, K	press., bar	CO_2 mole fraction L_1	CO_2 mole fraction L_2	molar vol, mL/(g-mol) v_{L_1}	molar vol, mL/(g-mol) v_{L_2}
CO_2–C_{12}	Q	235.66	10.58	0.577	0.974	103.2	44.1
CO_2–C_{10}	UCST	248.75	16.37	0.850	0.850	63.9	63.9
CO_2–C_{12}	Q	254.28	20.06	0.657	0.9749	104.7	47.5
CO_2–C_{12}	UCST	267.37	28.82	0.870	0.870	68.3	68.3
CO_2–C_{13}	Q	255.16	20.76	0.611	0.9842	117.2	46.2
CO_2–C_{13}	UCST	278.95	39.33	0.860	0.860	74.4	74.4
CO_2–C_{14}	Q	269.10	30.82	0.703	0.9821	105.9	50.6
CO_2–C_{14}	K	311.15	82.60	0.840		77.3	
CO_2–C_{15}	Q	270.40	31.94	0.680	0.9883	117.8	49.3
CO_2-C_{15}	K	309.41	80.22	0.788		98.1	
CO_2–C_{20}	Q	300.41	67.48	0.723	0.998	139.5	63.5
CO_2–C_{20}	K	305.31	75.49	0.704		131.6	

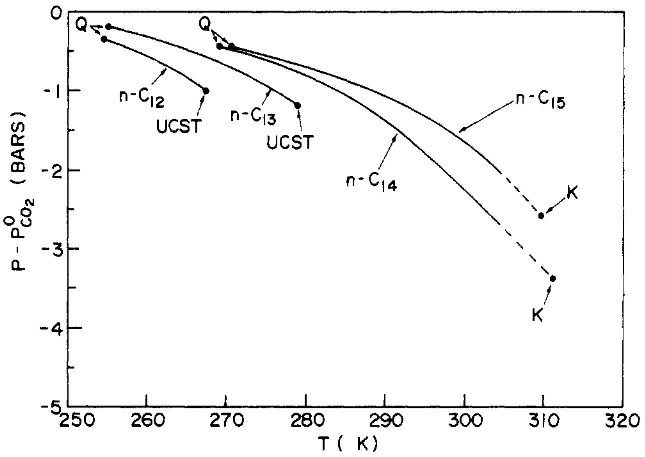

Figure 3. Deviation (smoothed) of the P vs. T curves of the L–L–V loci from the vapor-pressure curve of pure CO_2. $P^0_{CO_2}$ is the vapor pressure of pure CO_2. For temperatures exceeding the critical temperature of pure CO_2, the following equation for (hypothetical) $P^0_{CO_2}$ was employed: $P^0_{CO_2} = \exp(15.4437 - 1990.0/T) + 0.21136(T - 288.15)^2 - 18.47$, where $P^0_{CO_2}$ is in bar and T is in K.

decane (*2*) and CO_2–*n*-eicosane (*3*) systems. Note that the L_1–L_2–V locus decreases in extent in P–T space with increasing carbon number for those systems having a K point. For those systems having a UCST, the locus moves in P–T space to higher values of both variables and exhibits a lengthening, with increase of carbon number at least with respect to *n*-dodecane and *n*-tridecane.

All of the L_1–L_2–V loci studied exhibit an L_2 phase very rich in CO_2. Since the vapor phase is virtually pure CO_2, the L_1–L_2–V loci are close in P–T space to the L–V locus of pure CO_2. Figure 3 illustrates this proximity by showing P–$P^0_{CO_2}$ (smoothed) vs. T for each binary L_1–L_2–V system, where $P^0_{CO_2}$ is the vapor pressure of pure CO_2. The deviation of P from $P^0_{CO_2}$ is small and negative in all cases examined.

Glossary

K	K point, where L_2 and V phases become critical in the presence of L_1 phase
L	Liquid phase
L_1	liquid 1 phase
L_2	liquid 2 phase
P	pressure
T	temperature
UCST	upper critical solution (temperature) point where L_1 and L_2 phases become critical in presence of V phase
v	molar volume
V	vapor phase
x_i	mole fraction of species i

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Activities of Gallium–Thallium Components Determined by Vapor-Pressure Data

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The thallium activity in liquid Ga–Tl alloys was determined at 1000 K from vapor-pressure data. Mixing thermodynamic parameters of both components were evaluated and compared with those reported in the literature. A quadratic formalism for the activity coefficients and the enthalpic functions of the alloy components were derived.

Introduction

In order to complete the systematic investigation of the binary systems having as constituents Ga, Zn, and Tl (*1*, *2*) for taking these results into consideration for a future ternary system study and in connection with the use of thallium alloys as molecular sources of Tl in thermodynamic equilibria involving this constituent (*3*), we have determined the activities of the

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