where t represents the temperature in °C. The densities calculated from the above equations are given in Table I for comparison with observed values.

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Heterogeneous Phase Behavior of Carbon Dioxide in *n*-Hexane and *n*-Heptane at Low Temperatures

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The phase behavior of carbon dioxide in *n*-hexane and *n*-heptane was determined from 216.56°K to the eutectic point. Both systems exhibited partial miscibility phenomena in the upper range of the solubility curve. In the carbon dioxide–*n*-hexane system, the miscibility gap was metastable, and the upper critical solution temperature was determined as 213.7°K by careful subcooling. In the carbon dioxide–*n*-heptane system, the miscibility gap was stable and extended approximately 7°K above the normal solubility curve. The conjugate phase loci were intersected by the normal solubility curve, where L_1-L_2-S_1-V quadruple point was obtained. At the lower ends of the normal solubility curves, another quadruple point (L_2-S_1-S_2-V) or eutectic point was found for both systems. Normal solubility curves as well as the conjugate phase loci were correlated with the Wilson equation with a good predictive accuracy.

Experimental solubility of solid carbon dioxide in light hydrocarbons determined by Jensen (*5*) and in heavy hydrocarbons investigated by Im (*4*) shows that a definite tendency toward partial miscibility with heavier hydrocarbon solvents, as indicated by the increasingly flat solubility curve in the upper range, is characteristic of partially miscible systems as pointed out by Ricci (*8*). Francis (*2*) determined that *n*-heptane forms a stable miscibility gap with carbon dioxide and has an upper critical solution temperature of −51°C. He also predicted a miscibility gap for the carbon dioxide–*n*-hexane system by extrapolating the locus of critical solution temperatures of carbon dioxide–*n*-hexane–acetone system to zero acetone concentration and, in this manner, estimated its critical solution temperature as −61°C. However, no liquid-liquid equilibrium data have been reported for these systems.

That partial miscibility phenomenon was found in the methane–*n*-heptane system by Kohn (*6*) lends strong support to the likelihood that these two systems would form two partially miscible liquid phases in some portion of the solubility curves.

EXPERIMENTAL

A detailed description of the experimental equipment and procedure is given elsewhere (*4*). Briefly, phase boundaries along the miscibility gap as well as solid-liquid-vapor loci were determined by analyzing phase samples withdrawn from an equilibrium cell maintained at a given temperature, or when phase sampling was impracticable, by measuring the equilibrium temperature of a mixture of known composition. A schematic view of the phase equilibrium apparatus is shown in Figure 1. Constant temperature was provided in an air bath with liquid nitrogen as the refrigerant. The bath temperature was measured by a calibrated platinum resistance thermometer. Although the calibration accuracy of the thermometer was better than ±0.1°K, the maximum uncertainty in temperature measurements was reported as ±0.2°K owing to a small thermal gradient present in the bath.

Pressure was measured by a calibrated Heise gage whose accuracy was ±0.03 atm. Phase samples were analyzed on an F&M Model 720 gas chromatograph by use of a $^1/_4$-in. diameter, 5-ft long column packed with 5% squalane on Chromosorb W. To prevent two-phase formation during sample injection, a minute amount of sample was withdrawn into a sample trap under the equilibrium pressure and subsequently flashed into a bigger copper bomb attached to the sample trap. To assure complete vaporization of the sample, the whole sampling apparatus was heated in a conditioning oven connected to the carrier gas line so that sample injection could be carried out without a temperature change in the sample.

Hydrocarbons used were research grades furnished by Phillips Petroleum Co., and the carbon dioxide was Coleman Instrument grade obtained from Matheson Gas Products, Inc. Stated purity for all fluids was better than 99.9 mol %, confirmed by a laboratory analysis.

System fluids were charged into a glass equilibrium cell. After temperature control was obtained, 1 to 2 hr were allowed to attain equilibrium conditions. For the miscibility gap locus determination, the liquid phase to be sampled

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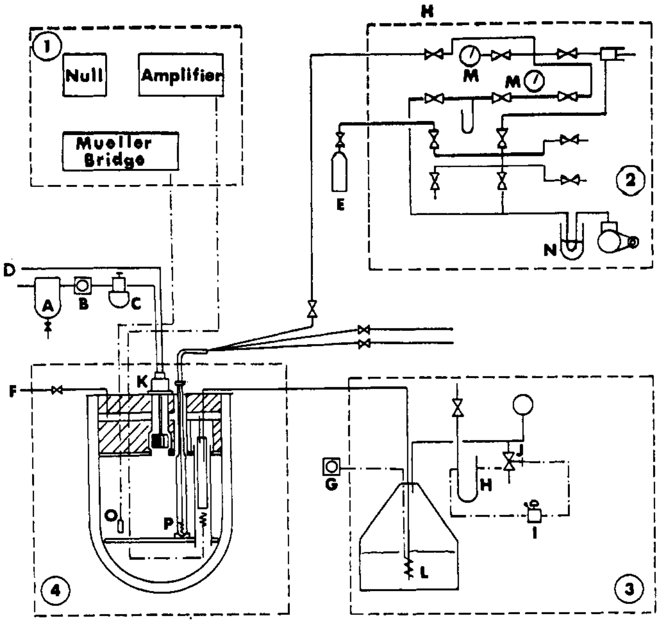

Figure 1. Phase equilibrium apparatus

1. Temperature control
2. Gas mixing and charging
3. Liquid nitrogen flow control
4. Low-temperature bath
A. Water trap
B. Air flow regulator
C. Air motor oiler
D. Air motor exhaust
E. Pure gas cylinder
F. LN_2 exhaust
G. Variac
H. Manometer
I. Overpressure alarm
J. Solenoid valve
K. Air motor
L. 100-liter dewar
M. Heise gages
N. LN_2 trap
O. Thermometer
P. Equilibrium cell

was created as large as possible compared to the other liquid phase to minimize interfacial contamination during sampling. For determination of the normal solubility curve or L_2-S_1 locus, phase sampling was done under its own saturation pressure down to slightly above 1 atm. When the saturation pressure was below the barometric pressure, the cell was pressurized with pure hydrocarbon to approximately 80 psia to force the liquid sample out.

The effect of pressure on solid solubility calculated was practically negligible, confirmed also experimentally. For the hydrocarbon-to-eutectic leg of the solubility curve or L_2-S_2 locus, freezing points were measured for prepared solutions of known compositions and determined by a copper-constantan thermocouple placed inside the cell and calibrated against triple points of pure hydrocarbons and carbon dioxide. The accuracy of temperature measured was better than ±0.17°K, and the composition of prepared solutions was known to be within ±1.5%.

RESULTS

Carbon Dioxide-*n*-Heptane System. The miscibility gap in this system was relatively small, extending approximately 7°K above the normal solubility curve. The upper critical solution temperature was determined as 222.6°K by observing the appearance or disappearance of the second liquid phase, which upon agitation coalesced into a separate liquid phase with a clearly visible phase boundary. This value of the upper critical solution temperature confirmed the previous measurement by Francis (*2*). The miscibility gap intersected the normal solubility curve where it formed a L_1-L_2-S_1-V quadruple point, an invariant point. Because of this interruption of the miscibility gap, the lower critical solution temperature was not defined. Figure 2 shows the miscibility gap and the L_1-L_2-S_1-V quadruple point.

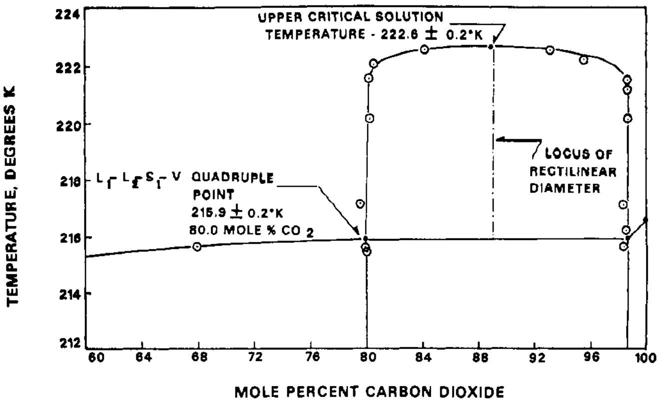

Figure 2. Miscibility gap in carbon dioxide–normal heptane system

The miscibility gap was of an unusual shape in that two conjugate phase loci were practically of constant composition up to within approximately 1°K of the consolute point, thus giving almost flat locus in the vicinity of the consolute point. Both conjugate phases are carbon dioxide rich, L_1 98.7 mol % and L_2 80.0 mol % carbon dioxide.

Since the miscibility gap is substantially symmetric, the upper critical solution point composition was determined as 89.0 ±0.5 mol % by the principle of rectilinear diameters. Within the temperature range investigated, the coexisting vapor phase was practically pure carbon dioxide, as expected from the wide disparity in vapor pressures of two components.

The L_1-L_2-S_1-V quadruple point temperature was estimated graphically as 215.9°K by extrapolating the L_2-S_1 locus and determining its intersection with the conjugate phase locus. The accuracy of this procedure was checked by plotting saturation pressures of the two-liquid phase region and the L_2-S_1 locus against the reciprocal of absolute temperature. The saturation pressure locus of the partially miscible region had a slope slightly but distinctly different from that of the normal solubility curve, and their intersection gave the quadruple point temperature at 215°K. At the lower end of the L_2-S_1 locus, another quadruple point or eutectic point was found. The eutectic temperature was measured directly as 181.75°K, and the eutectic composition was determined as 5.1 mol % carbon dioxide by slight extrapolation of the experimental L_2-S_1 locus.

Carbon Dioxide-*n*-Hexane System. The characteristic inverse-S shape of the normal solubility curve and tremendous jump of the solubility of approximately 23 mol % for a temperature change of 0.5°K at 215°K leads one to

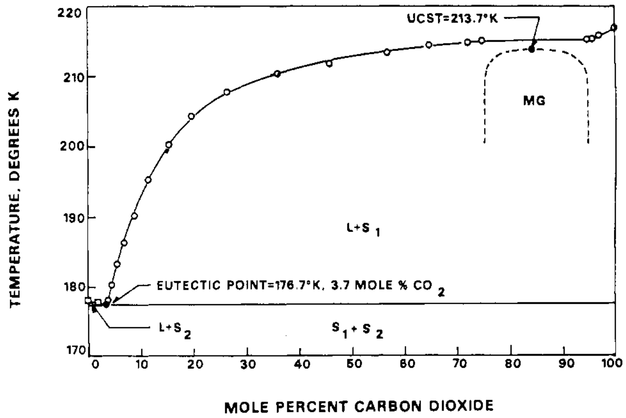

Figure 3. Condensed phase diagram for carbon dioxide–normal hexane system

Table I. Comparison of Correlations for Carbon Dioxide–Normal Hexane System Solubility Curve

T, °K	P, atm	Exptl x_{CO_2}	2-Parameter Wilson	3-Parameter Wilson	Scatchard-Hamer	Scatchard-Hildebrand
215.7	4.73	0.9723	0.9728	0.9726	0.9819	0.9678
215.2	4.63	0.9526	0.9475	0.9468	0.9727	0.3647
215.0		0.9514	0.9374	0.9364	0.9700	
214.9	4.49	0.7506	0.9258	0.9243	0.9672	0.3581
214.7		0.7252	0.9072	0.9047	0.9636	0.3538
214.2	4.32	0.6510	0.8393	0.8318	0.9543	0.3435
213.2	4.02	0.5722	0.6479	0.6338	0.9343	
211.7	3.78	0.4627	0.4780	0.4694	0.8948	0.2984
210.2	3.46	0.3593	0.3865	0.3810	0.1453	0.2752
207.7	2.86	0.2662	0.2947	0.2916	0.1322	0.2412
204.2	2.18	0.1990	0.2177	0.2161	0.1162	0.2013
200.2	1.16	0.1544	0.1621	0.1613	0.1005	0.1640
195.2	1.11	0.1177	0.1162	0.1158	0.0839	0.1265
190.2	0.74	0.0905	0.0849	0.0848	0.0699	0.0971
186.2	0.48	0.0681	0.0665	0.0664	0.0602	0.0781
183.2	0.37	0.0569	0.0554	0.0554	0.0537	0.0661
180.2	0.28	0.0457	0.0461	0.0461	0.0478	0.0558
178.2	0.23	0.0409	0.0408	0.0408	0.0441	0.0497
177.2	0.21	0.0382	0.0384	0.0384	0.0424	0.0468
Mean diff, mol %			−0.0360	−0.0334	−0.0567	0.1097
Std dev of mean			0.0679	0.0665	0.1739	0.1880
% Mean			−5.923	−5.359	−2.1047	9.08
Std dev of % mean			10.195	9.923	39.08	29.80

suspect that this system may also form a miscibility gap. However, according to the prediction of Francis (*2*), the consulute point estimated would place the gap below the normal solubility curve, implying a metastable state. Although Francis was unable to create the phase separation experimentally, the appearance of the second liquid phase was actually induced by subcooling under a carefully controlled condition, and the upper critical solution temperature was determined in the manner described for carbon dioxide–*n*-heptane system as 213.7°K, 1.7°K higher than predicted by Francis (*2*).

Unfortunately, all attempts to withdraw samples to define the two-liquid region failed owing to an extremely unstable condition in which two liquid phases coexist. A slight agitation caused instantaneous destruction of two liquid phases into a homogeneous phase. Nevertheless, from the shape of the normal solubility curve and the knowledge of the partial miscibility behavior of carbon dioxide–*n*-heptane system, the submerged gap can be constructed at least qualitatively (Figure 3).

Submerged miscibility gaps exist in other systems such as the salicylic acid–water system (*10*). Ricci (*8*) concluded from the study of systems having a metastable two-liquid region that the inverse-S shaped solubility curve is a common characteristic among these systems and that a rough proportionality exists between the flattening of the solubility curve and the closeness of the gap to the normal solubility curve. A eutectic point was also found in the carbon dioxide–*n*-hexane

Table II. Comparison of Correlations for Carbon Dioxide–Normal Heptane System Solubility Curve

T, °K	P, atm	Exptl x_{CO_2}	3-Parameter Wilson	Scatchard-Hildebrand	Scatchard-Hamer
215.6		0.6801		0.2852	0.9816
215.2	4.70	0.5810	0.5351	0.2782	0.9730
214.2	4.32	0.4440	0.4488	0.2639	0.9548
211.7	3.78	0.2908	0.3339	0.2318	0.8948
210.2	3.33	0.2592	0.2906	0.2146	0.2385
207.2	2.65	0.2152	0.2287	0.1840	0.2088
204.2	2.14	0.1737	0.1851	0.1577	0.1844
200.2	1.57	0.1544	0.1430		0.1574
195.2	1.11	0.1108	0.1056	0.1035	0.1300
190.2	0.72	0.0798	0.0787	0.0744	0.1074
185.2		0.0608	0.0588	0.0560	0.0886
183.2	0.41	0.0550	0.0523	0.0498	0.0819
182.2		0.0519	0.0493	0.0469	0.0788
Mean diff, mol %			−0.0030	0.0678	−0.1624
Std dev of mean			0.0212	0.147	0.2173
% Mean			−0.5427	21.02	−50.277
Std dev of % mean			7.3435	61.56	57.2782

Conjugate phase compositions

T, °K	P, atm	L_1, x_{CO_2}	L_2, x_{CO_2}
222.6[a]	6.40	0.8900	0.8900
222.5		0.9320	0.8430
222.2	6.26	0.9560	
222.0			0.8060
221.5	6.11	0.9870	0.8030
221.2		0.9870	
220.2	5.75	0.9870	0.8030
217.2		0.9840	0.9760
216.2		0.9860	
215.9[b]	4.695	0.9870	0.8000
215.6	4.69	0.9840	0.8000
215.4			0.8010

[a] UCST. [b] L_1-L_2-S_1-V quadruple point.

Table III. Parameters and Constants for Correlations

Wilson equations	CO_2-*n*-C_6H_{14}	CO_2-*n*-C_7H_{16}
2-Parameter model		
$\lambda_{12} - \lambda_{11}$	936.70	
$\lambda_{21} - \lambda_{22}$	620.78	
3-Parameter model		
c	1.005	1.0446
$\lambda_{12} - \lambda_{11}$	931.05	932.02
$\lambda_{21} - \lambda_{22}$	625.42	1225.00
Scatchard-Hamer		
A	2.1197	2.0606
B	1.7117	1.7188
Hildebrand-Scatchard		
l_{12}	0.0886	0.0946

Units for parameters are: Wilson parameters = cal/g-mol except c which is dimensionless. All other constants are dimensionless.

Table IV. Calculations for Miscibility Gap Prediction

T, °K	Saturation press, atm	CO_2 vapor press, atm	Ln $(f^{\nu o}/f^{\nu o *})$	x_1'	Ln γ_1'	x_1''	Ln γ_1''
222.60[a]	6.40	6.59	0.0293	0.890	0.14588		
222.16	6.26	6.47	0.0335	0.803	0.25286	0.987	0.04655
221.50	6.11	6.30	0.0306	0.803	0.24995	0.987	0.04304
220.16	5.75	5.96	0.0356	0.803	0.25496	0.987	0.04864
218.16	5.24	5.48	0.0438	0.801	0.26569	0.987	0.05688
217.16	4.94	5.24	0.0598	0.796	0.28791	0.984	0.07588
215.94[b]	4.70	4.97	0.0575	0.800	0.28068	0.987	0.07062
215.63	4.69	4.91	0.0450	0.800	0.26815	0.984	0.06113

[a] Upper critical solution temperature. [b] L_1-L_2-S_1-V quadruple point.

Table V. Predicted Miscibility Gap in Carbon Dioxide–*n*-Heptane System

			L_2, mol % CO_2		L_1, mol % CO_2	
T, °K	$\Lambda_{12} \times 10^6$	$\Lambda_{21} \times 10^2$	Exptl	Calcd	Exptl	Calcd
222.47			84.30	82.10	93.20	98.60
222.16	0.689	−0.889	80.30	82.00	98.70	98.70
221.50	0.637	−0.847				
220.16	0.707	−0.909	80.30	78.00	98.70	98.70
219.16			80.30	76.60	98.70	98.60
218.16	0.806	−0.974				
217.16	0.991	−1.238				
215.94	0.832	−1.044	80.00	68.50	98.70	98.50

system and was experimentally determined as 176.7°K and 3.7 mol % carbon dioxide.

CORRELATIONS

Correlation of normal solubility data was attempted with the Wilson (*11*), Hildebrand-Scatchard (*3*, *7*), and Scatchard-Hamer (*9*) equations. The experimental activity coefficient of carbon dioxide, γ_1, was calculated from the thermodynamic relationship

$$\Delta F_1{}^f = \left| -RT \ln \gamma_1 x_1 = \Delta S_1{}^f \right|_{T_p} (T_p - T) + \int_{T_p}^{T} \Delta C_p dT - T \int_{T_p}^{T} (\Delta C_p/T) dT$$

where ΔC_p, the difference between heat capacities, was obtained by extrapolation of normal liquid data into the subcooled region.

Comparison of experimental and calculated solubility data is given in Tables I and II, and experimental parameters are listed in Table III. Of the three equations tested, the Wilson equation in 3-parameter form gave best results for both systems with the average deviation 5% in the *n*-hexane and 0.5% in the *n*-heptane systems.

The conjugate phase locus was also correlated with the 3-parameter Wilson equation by means of the phase instability equations and the Plank's equation of state (*1*). The experimental liquid-liquid equilibrium data are compared against calculated results in Tables IV and V.

ACKNOWLEDGMENT

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NOMENCLATURE

A, B = constants in Scatchard-Hamer equation
c = third parameter in Wilson equation, independent of temperature
l_{12} = characteristic constant in Hildebrand-Scatchard equation according to modification by Preston and Prausnitz (*7*)
L_1, L_2 = liquid phases, L_1 richer in carbon dioxide than L_2
f_1^{ν} = fugacity of carbon dioxide in vapor phase, atm
$f_1^{\nu o}$ = fugacity of pure carbon dioxide vapor, atm
P = system pressure, atm
R = gas constant
S_1, S_2 = pure carbon dioxide and hydrocarbon solids, respectively
T = temperature, °K
T_p = triple point temperature of carbon dioxide, 216.56°K
V = vapor phase
x_i = composition of component i in liquid phase, mole fraction
γ_1 = activity coefficient of carbon dioxide in liquid phase
ΔC_p = difference in specific heat between solid and liquid carbon dioxide, cal/g-mol
$\Delta F_1{}^f$ = free energy of fusion of carbon dioxide, cal/g-mol
$\Delta S_1{}^f$ = entropy of fusion of carbon dioxide, cal/(g-mol)-(°K)
Λ_{ij} = adjustable parameters in Wilson equation
$\lambda_{ij} - \lambda_{ii}$ = constants in Wilson equation, originally assumed temperature independent, cal/g-mol

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