Partial Miscibility Behavior of the Ternary Mixture Carbon Dioxide + *n*-Tetradecane + Methanol

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The liquid−liquid−vapor (llg) partial miscibility behavior of the mixture carbon dioxide + *n*-tetradecane + methanol was experimentally studied by use of a visual cell (stoichiometric) technique. Phase compositions and molar volumes of the two liquid phases in equilibrium are reported as functions of temperature and pressure within the llg region. The addition of the cosolvent methanol extends the three-phase llg region in pressure−temperature space from the binary carbon dioxide + *n*-tetradecane llg locus downward in pressure, toward the vapor pressure curve of the cosolvent methanol. The three-phase region is bounded from above by an upper critical end point (l−l=g) locus, which extends from the binary llg locus to a lower critical end point (l=l−g) locus, which bounds the region at lower pressures. The cosolvent methanol significantly enhances the amount of the solute tetradecane present in the second (carbon-dioxide-rich) liquid phase.

Introduction

During the past two decades, our group has undertaken the experimental study of liquid−liquid−vapor (llg) phase equilibria in well-defined binary and ternary systems. These systems were typically composed of one or more gas solvents (e.g., carbon dioxide, ethane, propane, nitrous oxide, and/or xenon) and one or more relatively nonvolatile solutes chosen from a homologous series of *n*-alkanes, *n*-alkylbenzenes, and/or 1-alkanols. The primary goals of these studies were to map out the patterns of the multiphase equilibria of these prototype mixtures in thermodynamic phase space and to generate data that would support the prediction of phase equilibria within and near regions of llg partial immiscibility.

Successful supercritical extraction at temperatures near and above the critical temperature of a gas solvent is often accompanied by the presence of llg phase equilibria at lower temperatures (Hwang et al., 1978; Lansangan et al., 1987), be it actual or metastable (masked by the formation of a solid solute phase). Therefore, models that describe supercritical extraction should be capable of describing llg phase equilibria as well.

Additionally, there is the attractive prospect of carrying out *subcritical* extraction in an llg configuration, wherein a solute is selectively removed from the solute-rich liquid phase by the gas-solvent-rich phase in the presence of a gas-solvent-rich vapor phase. Compared to supercritical extraction, subcritical extraction would operate at more modest pressures and temperatures.

In several earlier studies our group has demonstrated that substantial selectivity between the two liquid phases in an llg system can be obtained between solutes of different molecular structure. For example, very favorable selectivity between solutes was found by our group in the llg subcritical systems carbon dioxide + *n*-tetradecane + 1-decanol (Patton et al., 1993) and ethane + *n*-docosane + 1-decanol (Patton and Luks, 1993). At the same time, the quantities of solutes present in the solvent-rich liquid phase are not especially large, with gas-solvent concentrations often exceeding 98 mol %. Investigators of supercritical extraction processes have addressed the problem of enriching the extract phase in the solute, and the addition of a modifier (*cosolvent*) to the extraction system has been carried out with some success. In the case of the gas solvent carbon dioxide, the cosolvent is generally a lighter molecular species of considerable dipole moment such as methanol (1.7 D) or acetone (2.88 D).

In this study, we will examine the effect of the cosolvent methanol on the llg phase equilibria of the binary mixture carbon dioxide + *n*-tetradecane. The mixture carbon dioxide + *n*-tetradecane has been studied before by both us and other groups as an llg system (Laugier et al., 1990; van der Steen et al., 1989; Hottovy et al., 1981). Of specific interest are the potential enhancement of the presence of the *n*-tetradecane in the carbon dioxide-rich liquid phase by the presence of methanol in the system, and the effect of the methanol on the growth of the three-phase llg region.

The llg phase equilibria of the ternary mixture carbon dioxide + *n*-tetradecane + methanol were studied using a visual cell (”stoichiometric”) experimental technique. The boundaries of the llg region were mapped out in pressure−temperature space, and then the compositions and the molar volumes of the two liquid phases were found along the 298.15 and 303.15 K isotherms.

Experimental Apparatus and Procedure

Fall and Luks (1984) and Jangkamolkulchai and Luks (1989) give a detailed description of the experimental apparatus. The procedures for performing the llg studies are described by Fall et al. (1985) and Jangkamolkulchai and Luks (1989). The experimental apparatus employs a stoichiometric approach wherein known amounts of *n*-tetradecane and methanol are added to a volumetrically calibrated visual (glass) equilibrium cell. The total volume of the cell is typically 7−9 cm^3. The cell vapor space is thoroughly flushed with carbon dioxide gas, after which measured amounts of the carbon dioxide gas are added to the cell from a high-pressure bomb. The cell contents are

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brought to equilibrium with a magnetically actuated steel ball stirrer mechanism. With the use of mass balances, the compositions and molar volumes of the phases in a ternary llg system at a given temperature and pressure can be determined from “conjugate” measurements.

Earlier studies (Lam and Luks, 1991; Patton et al., 1993) indicated that the presence of methanol and *n*-tetradecane in the vapor phase is negligible. Therefore, the mass balance calculations required a set of conjugate runs in which the l_1 and l_2 phases were respectively dominant in terms of volumetric fraction. l_1- and l_2-dominant run data at a specific temperature and pressure enabled quantitative assessment of the compositions and molar volumes of these phases. Since the vapor phase was assumed to be pure carbon dioxide, its stoichiometry was calculated from tables (Angus et al., 1976) rather than measured here.

The visual cell temperature was measured with a Pt-resistance thermometer to an estimated accuracy of ±0.02 K. The thermometer was calibrated against a Leeds and Northrup standard Pt-resistance thermometer in the laboratory to ±0.01 K IPTS-68. Pressures were measured to ±0.07 bar with pressure transducers that were frequently calibrated with a Ruska (Model 2400-601) dead-weight gauge. Phase volumes in the calibrated visual cell were determined with the aid of a cathetometer to an accuracy of at least 0.01 cm^3.

Materials

The methanol and *n*-tetradecane were purchased form Alfa Aesar (Johnson Mathey Co.). The methanol was Ultrapure HPLC Grade with a stated purity of 99.8+%. The *n*-tetradecane had a stated purity of 99%. Chromatographic analysis indicated purities consistent with these stated purities. These chemicals were used without further purification.

The carbon dioxide was purchased from Air Products and Chemicals, Inc. as “Coleman Grade” with a stated purity of 99.99 mol %. The carbon dioxide was first transferred to an evacuated storage bomb immersed in an ice bath. The vapor phase was vented to remove any light impurities. The purity was verified by liquefying the carbon dioxide at 298.15 K. The vapor pressure at this temperature was within 0.04 bar of that reported by Vargaftik (1975). In addition, the critical temperature and pressure were within 0.06 K and 0.07 bar of those reported by Vargaftik (1975).

Results

In Figure 1, portions of the boundaries of the llg surface of the ternary system carbon dioxide + *n*-tetradecane + methanol are shown. Their points are given in Table 1. The surface extends from the binary llg locus of carbon dioxide + *n*-tetradecane downward in pressure with the addition of the third component methanol (toward the methanol vapor pressure curve). The surface is terminated from above by an upper critical end point locus (UCEP or l−l=g) and from below by a lower critical end point locus (LCEP or l=l−g). These two loci would eventually intersect at a tricritical point (not shown). The l=l−g locus marks the termination of the llg region due to sufficiently high concentrations of methanol relative to the *n*-tetradecane in the carbon dioxide-rich system; carbon dioxide + methanol does not exhibit llg partial miscibility (Lam et al., 1990). Also shown are points along the isopycnic (barotropic inversion) locus, where the mass densities of the two liquid phases in the llg system are identical. The boundary points were determinable to ±0.1 K and ±0.07 bar.

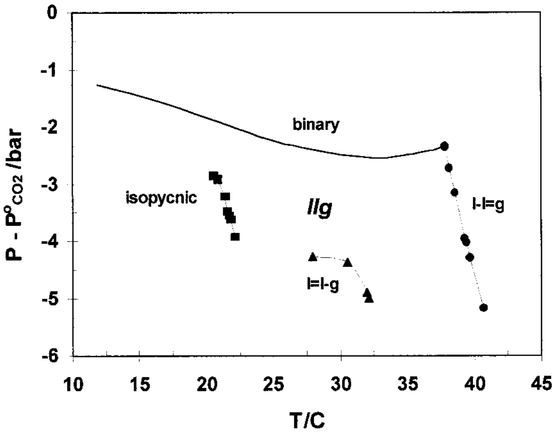

Figure 1. Deviation of the boundaries of the ternary llg surface from the vapor pressure curve for pure carbon dioxide in pressure−temperature space. $P^{\circ}_{CO_2}$ is the vapor pressure of carbon dioxide as represented by the correlation $\ln(P_r) = 6.58156(1 - 1/T_r)$. ■ = isopycnic (barotropic inversion) points; ▲ = l=l−g critical end points; ● = l−l=g critical end points.

Table 1. Temperature *T* and Pressure *P* Raw Data for the Liquid−Liquid−Vapor Boundary Loci for the Ternary Mixture Carbon Dioxide + *n*-Tetradecane + Methanol

UCEP (l−l=g)		LCEP (l=l−g)		isopycnic (barotropic inversion)	
T/K	*P*/bar	*T*/K	*P*/bar	*T*/K	*P*/bar
313.86	85.15	305.28	70.51	295.31	56.58
312.80	84.09	305.08	70.28	294.97	56.40
312.57	83.97	303.67	68.54	294.88	56.35
312.47	83.84	301.05	64.58	294.77	56.28
311.75	83.35			294.50	56.16
311.28	82.94			294.03	55.84
310.95	82.75			293.70	55.45

Table 2. Liquid-Phase l_1 and l_2 Compositions (Mole Fractions *x*) and Molar Volumes *v* As a Function of Pressure *P* for the Liquid−Liquid−Vapor Region of Carbon Dioxide + *n*-Tetradecane + Methanol at 298.15 K

l_1 phase				l_2 phase			
P/bar	$x(CO_2)$	$x(CH_3OH)$	*v*/(cm^3/mol)	*P*/bar	$x(CO_2)$	$x(CH_3OH)$	*v*/(cm^3/mol)
62.39	0.8326	0.0000	87.85	62.39	0.9655	0.0000	61.63
61.78	0.8345	0.0105	83.77	62.16	0.9648	0.0025	62.07
61.28	0.8479	0.0132	80.29	61.88	0.9613	0.0049	62.05
61.06	0.8502	0.0150	79.09	61.80	0.9588	0.0062	61.53
				61.60	0.9548	0.0081	62.18
				61.60	0.9549	0.0084	62.20
				61.01	0.9419	0.0149	62.44
				61.01	0.9410	0.0150	62.65

The llg data for the ternary system along the isotherms 298.15 and 303.15 K are given in Tables 2 and 3. Data for the isotherm 298.15 K are plotted in Figures 2 and 3. The ternary mole fractions are estimated to be accurate to ±0.004 and the molar volumes to ±0.6 cm^3/mol. These are conservative estimates, based on average absolute deviations (AADs) of the raw data from simple smoothed curves and our experience at being able to generate reproducible data using the stoichiometric technique in previous studies.

Discussion

As pointed out in the Introduction, one of the measures of a successful cosolvent is the enhancement of the capacity of the l_2 phase for the solute. Table 4 suggests that methanol is an effective cosolvent here. The molar concentration of the solute *n*-tetradecane is significantly increased

Table 3. Liquid-Phase l_1 and l_2 Compositions (Mole Fractions *x*) and Molar Volumes *v* As a Function of Pressure *P* for the Liquid−Liquid−Vapor Region of Carbon Dioxide + *n*-Tetradecane + Methanol at 303.15 K

l_1 phase				l_2 phase			
P/bar	$x(CO_2)$	$x(CH_3OH)$	$v/(cm^3/mol)$	*P*/bar	$x(CO_2)$	$x(CH_3OH)$	$v/(cm^3/mol)$
69.70	0.8391	0.0000	84.96	69.70	0.9675	0.0000	60.65
68.92	0.8420	0.0080	81.71	69.37	0.9717	0.0026	61.76
68.42	0.8503	0.0117	78.88	69.00	0.9679	0.0052	61.10
67.95	0.8545	0.0152	77.73	68.84	0.9659	0.0061	61.20
67.72	0.8574	0.0186	76.18	68.65	0.9617	0.0087	61.84
				67.91	0.9486	0.0158	61.45
				67.81	0.9473	0.0161	61.95
				67.68	0.9457	0.0172	62.38

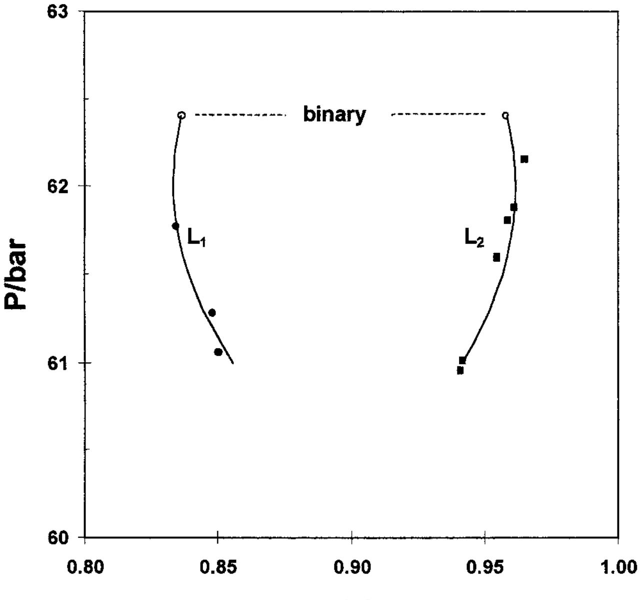

Figure 2. Pressure *P* as a function of mole fraction of carbon dioxide for the l_1 and l_2 phases for the liquid−liquid−vapor region of carbon dioxide + *n*-tetradecane + methanol at 298.15 K.

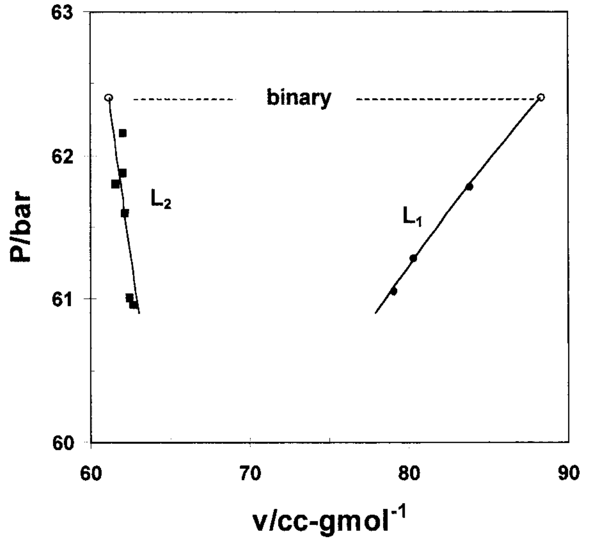

Figure 3. Pressure *P* as a function of molar volume *v* for the l_1 and l_2 phases for the liquid−liquid−vapor region of carbon dioxide + *n*-tetradecane + methanol at 298.15 K.

Table 4. Concentration *C* of *n*-Tetradecane and Mole Ratio of *n*-Tetradecane to Carbon Dioxide in Liquid Phase 2 As a Function of Pressure at the Temperatures 298.15 and 303.15 K for the Liquid−Liquid−Vapor Region of Carbon Dioxide + *n*-Tetradecane + Methanol

liquid phase 2 at 298.15 K			liquid phase 2 at 303.15 K		
P/bar	$10^4C(nC_{14})$/ $mol \cdot cm^{-3}$	$10^2r(nC_{14}/CO_2)$	*P*/bar	$10^4C(nC_{14})$/ $mol \cdot cm^{-3}$	$10^2r(nC_{14}/CO_2)$
62.39	5.5910	3.5688	69.70	4.1818	2.6213
62.16	5.2714	3.3917	69.37	4.1742	2.6531
61.88	5.4447	3.5143	69.00	4.3988	2.7768
61.80	5.6864	3.6491	68.84	4.5821	2.9033
61.60	5.9567	3.8789	68.65	4.7957	3.0841
61.60	5.8960	3.8405	67.91	5.7897	3.7505
61.01	6.9178	4.5853	67.81	5.9114	3.8659
61.01	7.0244	4.6770	67.68	5.9466	3.9224

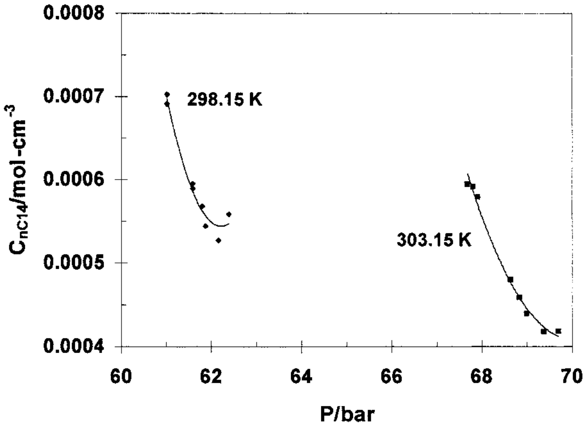

Figure 4. Molar concentration *C* of *n*-tetradecane in liquid phase 2 as a function of pressure *P* for the liquid−liquid−vapor region of carbon dioxide + *n*-tetradecane + methanol at 298.15 and 303.15 K.

as the ternary system enriches with methanol, both at 298.15 and 303.15 K. See Figure 4. This effect exceeds the effect of *n*-tetradecane concentration enhancement that one would expect as one approaches the l=l−g locus, at which points the l_2 phase becomes identical with the l_1 phase. The increase in the ratio of *n*-tetradecane-to-carbon dioxide is not as rapid as that of the *n*-tetradecane concentration *C*.

In a future study, we will be investigating the effect that a more polar cosolvent will have on the *n*-tetradecane concentration enhancement in a carbon dioxide-rich environment.

Glossary

AAD	average absolute deviation
C	molar concentration (mol/cm^3)
g	gas or vapor phase
LCEP	lower critical end point
l, l_1, l_2	liquid phases
l−l=g	a three-phase critical end point where the less dense liquid phase (l_2) and the vapor phase (g) are critically identical; also referred to as the UCEP
l=l−g	a three-phase critical end point where the two liquid phases (l_1 and l_2) are critically identical; also referred to as the LCEP
P	pressure
r	mole ratio of *n*-tetradecane to carbon dioxide
T	temperature
UCEP	upper critical end point
v	molar volume
x	mole fraction

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