

# Three-Phase Liquid–Liquid–Vapor Equilibria of the Binary Mixture Carbon Dioxide + 1-Methylnaphthalene

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The liquid–liquid–vapor (llg) partial miscibility behavior of the mixture carbon dioxide + 1-methylnaphthalene was experimentally studied by use of a visual cell (stoichiometric) technique. Pressure, phase compositions, and molar volumes of the two liquid phases in equilibrium are reported as a function of temperature along the llg locus. The three-phase locus is terminated above by an upper critical end point (l–l=g) at 308.81 K and 79.30 bars and below by a four-phase quadruple point (sllg) at 219.05 K and 5.68 bar and has an isopycnic inversion at approximately 245.5 K and 15.6 bar.

## 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, 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.

The study of these systems has relevance to supercritical extraction at temperatures near and above the critical temperature of a gaseous solvent. Also, there is the possibility to carry out subcritical extraction in an llg phase equilibrium 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.

Systems promising successful supercritical extraction are often accompanied by a regime of llg-phase equilibria at lower temperatures,<sup>1,2</sup> which could be either actual or metastable (masked by the formation of a solid solute phase). Therefore, models to describe supercritical extraction should be capable of describing llg-phase equilibria as well.

There has been interest in the phase equilibria of the highly aromatic species 1-methylnaphthalene as a prototype solute in equilibrium with the solvent gas carbon dioxide in several different contexts, including supercritical extraction: (1) Sebastian et al.<sup>3</sup> reported the *P*–*x*–*y* phase equilibrium data for carbon dioxide + 1-methylnaphthalene at temperatures of 189.9, 270.3, 350.4, and 430.4 K at pressures up to 50.8 atm. (2) Chai and Paulaitis<sup>4</sup> determined the Henry's Law constants for carbon dioxide dissolved in 1-methylnaphthalene in the temperature range 298.6 to 330.2 K. (3) Morris and Donohue<sup>5</sup> reported the *P*–*x*–*y* phase equilibrium data for carbon dioxide +

1-methylnaphthalene at temperatures of 353.15 and 413.15 K at pressures up to 144.5 bar. (4) Lee and Chao<sup>6</sup> reported the *P*–*x*–*y* phase equilibrium data for carbon dioxide + 1-methylnaphthalene at temperatures of 308.2, 318.2, and 328.2 K at pressures up to 240 bar. (5) Gregg and Radosz<sup>7</sup> studied the vapor–liquid-phase equilibria of the binary mixture carbon dioxide + 1-methylnaphthalene at temperatures of 50, 100, 150, 200, and 250 °C at pressures up to 159 bar. (6) Kim et al.<sup>8</sup> studied the vapor–liquid-phase equilibria of the binary mixture carbon dioxide + 1-methylnaphthalene at a temperature of 372.6 K at pressures up to 206.7 bar. (7) Chung and Shing<sup>9</sup> studied the vapor–liquid-phase equilibria of the binary mixture carbon dioxide + 1-methylnaphthalene at temperatures of 35 and 55 °C at pressures up to 278.1 bar.

There have also been a few ternary studies with the constituent binary mixture carbon dioxide + 1-methylnaphthalene, such as the vapor–liquid study<sup>10</sup> of the mixtures carbon dioxide + 1-methylnaphthalene + anisole and carbon dioxide + 1-methylnaphthalene + benzaldehyde, in which the additional components are present in lesser amounts relative to the 1-methylnaphthalene.

An analogous llg study to that reported in the present paper exists for the related system carbon dioxide + 2-methylnaphthalene.<sup>11</sup> They reported that the llg locus extends between two termini, the upper critical end point (UCEP, or l–l=g) at about 36.31 °C (309.46 K) and 79.14 atm (80.19 bar) and the quadruple point Q (sllg) at 9.10 °C (282.25 K) and 42.34 atm (42.90 bar). The llg locus of the carbon dioxide + 2-methylnaphthalene system is much shorter than the llg locus of carbon dioxide + 1-methylnaphthalene herein, since the normal melting point of 2-methylnaphthalene is 33.45 °C (306.60 K) compared to about –30.6 °C (242.6 K) for 1-methylnaphthalene. This melting point disparity gives the system carbon dioxide + 1-methylnaphthalene a much lower Q point temperature. Granted the existence of an llg regime for carbon dioxide + 2-methylnaphthalene, it is not surprising that one should exist for carbon dioxide + 1-methylnaphthalene as well. It is noted that Lee and Chao<sup>6</sup> correctly suggested the possible existence of an llg locus for carbon dioxide + 1-methylnaphthalene, based on their interpretation of the changes in the composition *x* as a function of pressure data at 308.2 K.

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**Table 1. Pressure  $P$ , Liquid-Phase  $l_1$  and  $l_2$  Composition (Mole Fractions  $x$ ), and Molar Volume  $v$ , as a Function of Temperature  $T$ , for the Liquid-Liquid-Vapor Locus of Carbon Dioxide + 1-Methylnaphthalene**

$T/K$	$P/\text{bar}$	$l_1$ phase		$l_2$ phase		comment
		$x(\text{CO}_2)$	$v/(\text{cm}^3\cdot\text{mol}^{-1})$	$x(\text{CO}_2)$	$v/(\text{cm}^3\cdot\text{mol}^{-1})$	
308.81	79.30					l-l=g
303.00	69.88			0.9865	61.4	l-l-g
298.13	62.46	0.4848	92.4	0.9851	58.3	l-l-g
293.14	55.81	0.4736	93.6	0.9808	55.5	l-l-g
288.14	49.61	0.4637	94.7	0.9793	53.5	l-l-g
283.15	43.99	0.4537	95.5	0.9781	51.9	l-l-g
278.15	38.81	0.4463	96.9	0.9775	49.9	l-l-g
273.15	34.15	0.4302	97.3	0.9761	48.9	l-l-g
268.15	29.88	0.4210	98.2	0.9752	47.6	l-l-g
263.15	25.98	0.4070	99.1	0.9720	46.8	l-l-g
258.15	22.50	0.3935	99.8	0.9752	46.0	l-l-g
253.16	19.37	0.3802	100.7	0.9755	45.2	l-l-g
248.16	16.57	0.3675	101.0	0.9720	44.6	l-l-g
245.48	15.59					l-l-g ( $\rho_{M,L1} = \rho_{M,L2}$ )
219.05	5.68					s-l-l-g

In this study, the llg phase equilibria of the binary mixture carbon dioxide + 1-methylnaphthalene were studied using a visual cell ("stoichiometric") experimental technique. Compositions and molar volumes of the  $l_1$  and  $l_2$  phases are reported along the llg locus, as well as its upper and lower termini, the UCEP point (l-l=g) and the Q point (sllg), respectively.

### Experimental Apparatus and Procedure

Fall and Luks<sup>12</sup> and Jangkamolkulchai and Luks<sup>13</sup> give a detailed description of the experimental apparatus. The procedures for performing the llg studies are described in refs 13 and 14.

The experimental apparatus employs a stoichiometric approach wherein a known weight of 1-methylnaphthalene is added to a volumetrically calibrated visual (glass) equilibrium cell. The total volume of the cell is typically 7 to 9 cm<sup>3</sup> and is known precisely. After the 1-methylnaphthalene is added, the cell vapor space is thoroughly flushed with carbon dioxide gas. It is assumed for *stoichiometric purposes only* that the presence of 1-methylnaphthalene in the vapor phase can be neglected. To strengthen this assumption, the volume (i.e., the molar amount) of the vapor phase is kept small in all measurements. Since the vapor phase is assumed to be pure carbon dioxide, its stoichiometry is calculated from tables (Angus et al.<sup>15</sup>) rather than measured.

Carefully measured amounts of the carbon dioxide gas are added to the cell from a high-pressure bomb. The cell contents are brought to thermal and mass flow equilibria by a magnetically actuated steel ball stirrer mechanism. At equilibrium, the liquid-phase volumes are measured using a cathetometer. Phase volumes in the calibrated visual cell were determined with the aid of a cathetometer to an accuracy of at least 0.01 cm<sup>3</sup>.

The compositions and molar volumes of the phases in a binary llg system at a given temperature and pressure can be determined from "conjugate" measurements denoted as unprimed and primed quantities below, with the volume and mass raw data being inserted into the following mass balances:

$$\begin{aligned}
 V_{11}c_{1-MN,11} + V_{12}c_{1-MN,12} &= N_{1-MN,feed} \\
 V_{11}c_{1-MN,11} + V_{12}c_{1-MN,12} &= N_{1-MN,feed} \\
 V_{11}c_{CO_2,11} + V_{12}c_{CO_2,12} &= \\
 N_{CO_2,feed} - N_{CO_2,vapor} + N_{CO_2,vapor-initial} & \\
 V_{11}c_{CO_2,11} + V_{12}c_{CO_2,12} &= \\
 N_{CO_2,feed} - N_{CO_2,vapor} + N_{CO_2,vapor-initial} &
 \end{aligned}$$

where  $V$ ,  $V$ ,  $N$ , and  $N$  are the liquid-phase volumes and the mole numbers from the two conjugate runs. The molar concentrations  $\{c_{i,j}\}$  are then calculated. A set of conjugate runs constitutes two runs at a specific temperature, in which the  $l_1$  and  $l_2$  phases are respectively dominant in terms of their volumetric fraction. By using the data from these two runs, the mass balances act as a lever principle that determines the compositions and molar volumes of these phases. Conjugate runs at a specific temperature are always replicated as a check on precision.

The visual cell temperature was measured with a Pt-resistance thermometer to an estimated accuracy of  $\pm 0.02$  K. The thermometer was calibrated against a Leeds and Northrup standard Pt-resistance thermometer in the laboratory, and temperatures are reported using the ITS-90 temperature scale. Pressures were measured to  $\pm 0.07$  bar with pressure transducers that were frequently calibrated with a Ruska (Model 2400-601) dead-weight gauge.

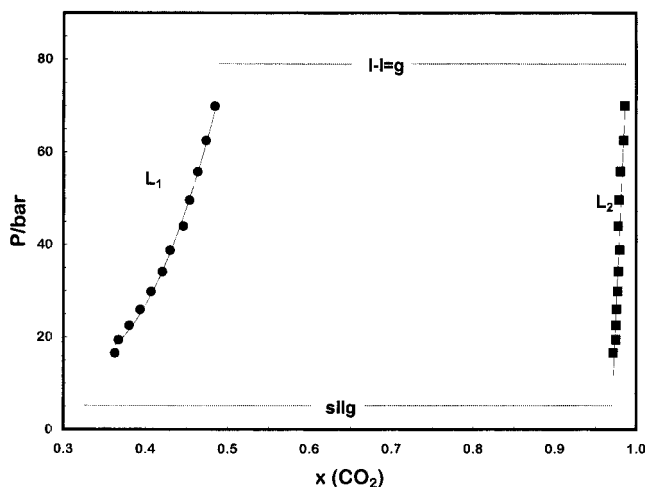
### Materials

The 1-methylnaphthalene was purchased from Aldrich Chemical Co. with a stated purity of 98 mol % and was 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.<sup>16</sup> In addition, the critical temperature and pressure were within 0.06 K and 0.07 bar of those reported by Vargaftik.<sup>16</sup>

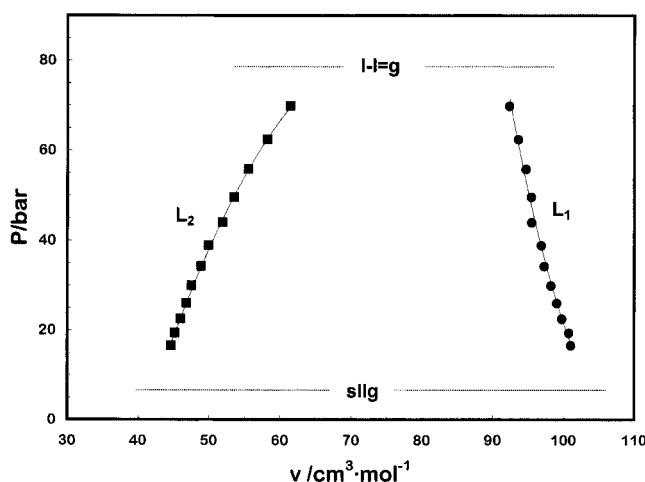
### Results

The llg data for the binary system are given in Table 1 and Figures 1 and 2. The llg locus of the binary system extends from its upper terminus, an upper critical end point l-l=g at 308.81 K and 79.30 bars, to its lower terminus, a four-phase sllg point at 219.05 K and 5.68 bars. The solid phase of the sllg point is assumed to be pure 1-methylnaphthalene; this quadruple point occurs at a temperature substantially below that of the pure 1-methylnaphthalene melting point, estimated by us to be at about  $-30.6 \pm 0.2$  °C (about 242.6 K).

As is often the case with carbon dioxide + hydrocarbon llg systems, there occurs an isopycnic (barotropic inversion) point, determined to be 245.48 K for carbon dioxide + 1-methylnaphthalene, below which temperature the mass density of the  $l_2$  phase is greater than that of the  $l_1$  phase.



**Figure 1.** Pressure  $P$  as a function of the mole fraction of carbon dioxide for the  $l_1$  and  $l_2$  phases for the liquid-liquid-vapor locus of the binary mixture carbon dioxide + 1-methylnaphthalene.



**Figure 2.** Pressure  $P$  as a function of the molar volume of the  $l_1$  and  $l_2$  phases for the liquid-liquid-vapor locus of the binary mixture carbon dioxide + 1-methylnaphthalene.

The temperature of this point is lower than that of typical isopycnic points observed with carbon dioxide and most hydrocarbons (e.g.,  $n$ -paraffins). The inversion of the  $l_1$  and  $l_2$  phases in the visual cell is caused by the density of the carbon dioxide-rich  $l_2$  phase exceeding that of the hydrocarbon-rich  $l_1$  phase upon cooling. Since the mass density of pure 1-methylnaphthalene is relatively high for a hydrocarbon, being nominally close to  $1 \text{ g}\cdot\text{cm}^{-3}$ , greater cooling of the llg system is required in order to reach the isopycnic point.

The mole fractions of the carbon dioxide are estimated to be accurate to  $\pm 0.004$  in phase  $l_1$  and  $\pm 0.002$  in phase  $l_2$ . The molar volumes are estimated to be accurate to  $\pm 0.8 \text{ cm}^3\cdot\text{mol}^{-1}$  for phase  $l_1$  and  $\pm 0.3 \text{ cm}^3\cdot\text{mol}^{-1}$  for phase  $l_2$ . 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

The extent of the carbon dioxide + 1-methylnaphthalene llg locus in terms of temperature (equivalently, pressure) is larger than has been seen with carbon dioxide and other hydrocarbons. 1-Methylnaphthalene demonstrates pro-

nounced partial miscibility with carbon dioxide (e.g.,  $x(\text{CO}_2)_{l_1} < 0.5$ ), as might be expected with such a large aromatic species; additionally, 1-methylnaphthalene has a relatively low melting point, due to its unique structure. In comparison, 2-methylnaphthalene has a melting point of 306.6 K.<sup>11</sup>

Despite the relatively low solubility of carbon dioxide in the  $l_1$  phase (hydrocarbon-rich phase) along the llg locus, the solubility of 1-methylnaphthalene in the  $l_2$  phase (carbon dioxide-rich phase) is on the order of 2 mol %, less than that of  $n$ -tetradecane (on the order of 3 mol %) but more than that of 1-decanol (on the order of 1 mol %). For these two hydrocarbons, carbon dioxide is significantly more soluble in the  $l_1$  phase.  $n$ -Tetradecane is the lightest  $n$ -paraffin to exhibit partial miscibility throughout the ambient temperature regime.

## Glossary

AAD = average absolute deviation

$c$  = molar concentration

$g$  = 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; herein, the UCEP

$N$  = moles

$P$  = pressure

$Q$  = quadruple point, or four-phase point; herein, the sllg point

$s$  = solid phase

sllg = a four-phase quadruple point consisting of a solid phase, two liquid phases, and a vapor phase

$T$  = temperature

UCEP = upper critical end point

$V$  = phase volume

$v$  = molar volume

$x$  = mole fraction

## Subscripts

$i$  = species

$j$  = phase

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