

# CORRELATION OF VAPOR-LIQUID EQUILIBRIA FOR CARBON DIOXIDE + HIGH-BOILING COMPONENT SYSTEMS USING SIMPLIFIED PERTURBED HARD CHAIN THEORY

YOSHIO IWAI, TATSUO MOROTOMI, NORIAKI HOSOTANI, YOSHIO KOGA AND YASUHIKO ARAI  
*Department of Chemical Engineering, Kyushu University, Fukuoka, 812-81*

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## Introduction

It is useful to correlate the high-pressure vapor-liquid equilibria for systems containing supercritical carbon dioxide in the process design of supercritical fluid extraction. The simplified perturbed hard chain theory (SPHCT) based on the hole theory was applied to correlate vapor-liquid equilibria for the supercritical carbon dioxide + high-boiling component systems. The SPHCT has an advantage because no critical property for high-boiling component is necessary to determine the characteristic parameters.

## 1. Simplified Perturbed Hard Chain Theory

The equation of state given by the SPHCT is shown as follows <sup>6)</sup>:

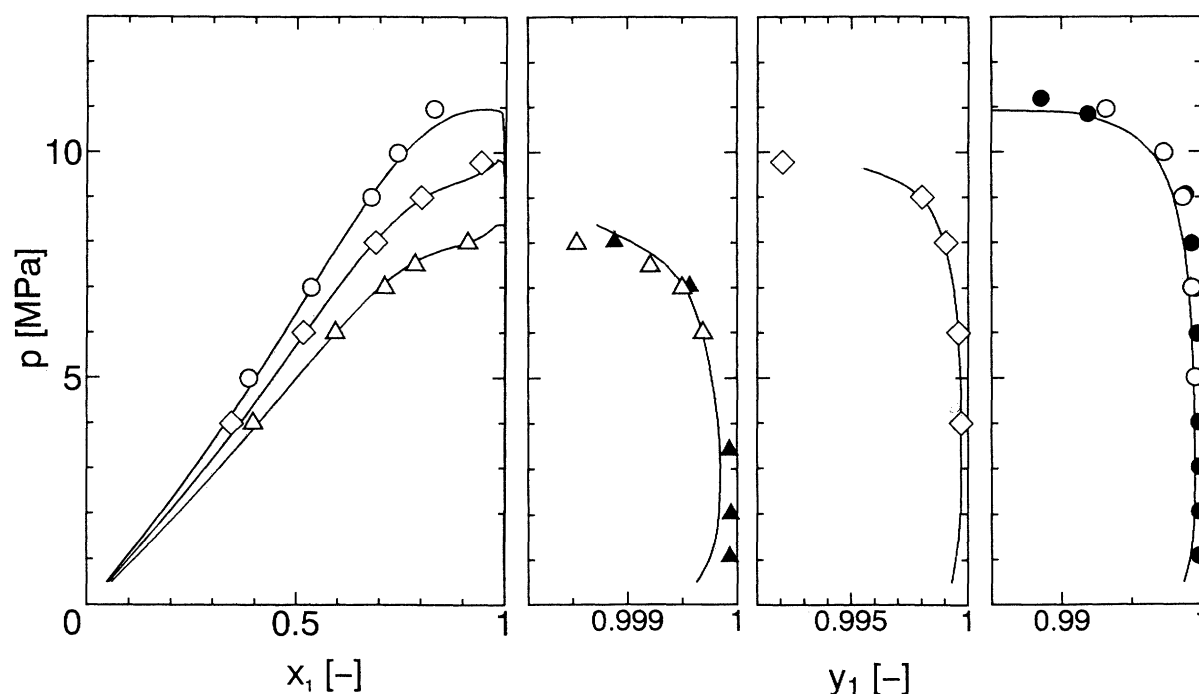
$$p = p^{\text{hc}} - RT \frac{Z_M \langle cv^* Y \rangle}{\langle v \rangle} \frac{\langle v + \langle cv^* Y \rangle \rangle}{\langle c \rangle} \quad (1)$$

$$Y = \exp(\varepsilon / 2c kT) - 1 \quad (2)$$

$$p^{\text{hc}} = \frac{RT}{v} \left( 1 + \langle c \rangle \frac{4\xi - 2\xi^2}{(1 - \xi)^3} \right) \quad (3)$$

$$\xi = \frac{\sqrt{2}\pi \langle v^* \rangle}{6v} \quad (4)$$

\* Received November 9, 1994. Correspondence concerning this article should be addressed to Y. Iwai



**Fig. 1** Correlation results for carbon dioxide (1) + linalool (2) system at 313.2, 323.2 and 333.2 K: (○) experimental data at 333.2 K<sup>3</sup>; (◇) 323.2 K<sup>3</sup>; (△) 313.2 K<sup>3</sup>; (●) 333.2 K<sup>9</sup>; (▲) 313.2 K<sup>9</sup>; (—) calculated results with  $k_{12} = 0.141$

**Table 1.** Characteristic Parameters for SPHCT

substance	$T_b$ (K)	$\varepsilon$ (J·mol <sup>-1</sup> )	$v^* \times 10^5$ (m <sup>3</sup> ·mol <sup>-1</sup> )	$c$
CO <sub>2</sub> *	194.7	1473.9	2.2000	1.255
CO <sub>2</sub> **		1612.5	1.4641	1.800
CO <sub>2</sub> ***		1579.5	1.4641	1.800
linalool*	471.2	4999.2	10.5673	3.106
methanol*	337.8	2921.6	5.6179	2.015
ethanol*	351.5	3099.1	6.0408	2.108
decane*	447.3	4563.2	9.5285	2.877
benzene*	353.3	3123.0	6.0976	2.121

\* Eqs. (10)-(13)

\*\* saturated properties

\*\*\* VLE

where  $p$  is the total pressure,  $p^{hc}$  is the hard chain pressure term,  $T$  is the absolute temperature,  $v$  is the molar volume,  $v^*$  is the close-packed volume,  $c$  is the number of external degrees of freedom,  $\varepsilon$  is the interaction energy parameter,  $Z_M$  is the maximum coordination number,  $k$  is the Boltzmann constant and  $R$  is the gas constant. The terms in angular brackets,  $\langle \dots \rangle$ , represent mixture properties. The following mixing rules can be used:

$$\langle c \rangle = \sum_i x_i c_i \quad (5)$$

$$\langle v^* \rangle = \sum_i x_i v_{ii}^* \quad (6)$$

$$\langle c v^* Y \rangle = \sum_{ii} x_i x_j c_i v_{ij}^* \left\{ \exp \left( \varepsilon_{ij} / 2c_i kT \right) - 1 \right\} \quad (7)$$

$$\varepsilon_{ij} = (1 - k_{ij}) \sqrt{\varepsilon_{ii} \varepsilon_{jj}} \quad (8)$$

$$v_{ij}^* = \left\{ \left( v_{ii}^{* \frac{1}{3}} + v_{jj}^{* \frac{1}{3}} \right) / 2 \right\}^3 \quad (9)$$

where  $k_{ij}$  is the interaction parameter between unlike molecules  $i$  and  $j$ , and treated as fitting parameters for the experimental results.

## 2. Characteristic Parameters

The parameters,  $\varepsilon$ ,  $v^*$  and  $c$ , for pure components are required. The linear behavior between each parameter and carbon number for the  $n$ -alkanes was reported by Kim *et al.*<sup>6</sup> In this work, in order to extend these parameters to other substances, the parameters for several compounds were correlated with the effective carbon number ( $ECN$ ) proposed by Georgeton and Teja<sup>2</sup>. The parameters,  $\varepsilon$ ,  $v^*$  and  $c$ , can be approximately correlated as linear functions of  $ECN$  as follows:

$$\varepsilon = 590.68 + 397.27 \times ECN \quad (10)$$

$$v^* = 6.4998 \times 10^{-7} + 9.4636 \times 10^{-6} \times ECN \quad (11)$$

$$c = 0.79146 + 0.20857 \times ECN \quad (12)$$

where  $ECN$  is defined by:

$$ECN[-] = -0.11630 - 0.019376 \times T_b + 1.1594 \times 10^{-4} \times T_b^2 - 1.549 \times 10^{-7} \times T_b^3 + 1.3513 \times 10^{-10} \times T_b^4 + 0.19102 \times T_b^{0.5} \quad (13)$$

These approximations are available for methanol, ethanol and benzene as well as  $n$ -alkanes.

**Table 2.** Correlation Results for Binary Systems Using SPHCT

System	<i>T</i> (K)	<i>p</i> (MPa)	<i>N</i>	<i>k</i> <sub>12</sub>	$\Delta x_1^*$	$\Delta y_1^{**}$	Ref.
CO <sub>2</sub> + linalool	313.2-333.2	4.0-10.2	30	0.141	0.00723	0.00033	3), 9)
CO <sub>2</sub> + methanol	298.2	0.2-6.1	21	0.131	0.02363	0.00508	4), 7)
CO <sub>2</sub> + ethanol	304.2	3.8-7.2	12	0.135	0.02065	0.00324	10)
CO <sub>2</sub> + decane	311.0-344.3	0.7-12.8	25	0.121	0.02511	0.00046	1), 3), 8)
CO <sub>2</sub> + benzene	313.2	1.5-7.8	9	0.088	0.00932	0.00384	5)

$$* \Delta x_1 = \frac{1}{N} \sum |x_{1, \text{calc}} - x_{1, \text{exp}}|$$

$$** \Delta y_1 = \frac{1}{N} \sum |y_{1, \text{calc}} - y_{1, \text{exp}}|$$

*N* : number of data

### 3. Correlation of Vapor-Liquid Equilibria

The vapor-liquid equilibria (VLE) of carbon dioxide + high-boiling component binary systems were correlated. The fugacity of the *i*-th component in the mixture, required in the phase equilibrium calculation, can be readily derived thermodynamically by Eqn. (1) and the mixing rules, Eqs. (5) to (9). First, the carbon dioxide + linalool system, for which VLE were measured by the authors<sup>3)</sup>, was examined. The characteristic parameters of both carbon dioxide and linalool can be estimated by using Eqs.(10) to (13). The normal boiling points for carbon dioxide and linalool are 194.7 and 471.2 K, respectively. It is found that VLE for the binary system could not be correlated well even though the interaction parameter, *k*<sub>*ij*</sub>, was introduced. As a reason for this discrepancy, it should be noted that the sublimation temperature for carbon dioxide under atmospheric pressure (194.7 K) was adopted as the normal boiling point. Therefore, the parameters for carbon dioxide were redetermined by using the saturated properties and applied to correlate VLE for the carbon dioxide + linalool system. The correlation effectiveness in the low pressure region is found to be good. However, VLE under high pressure could not be correlated. Finally, the parameters for carbon dioxide were determined to give a precise fit for VLE. In this case, the parameters for linalool were given by Eqs. (10) to (13). As shown in Fig. 1, VLE for the carbon dioxide + linalool system are well correlated up to the critical point of the mixture and it should be noted that the interaction parameter, *k*<sub>*ij*</sub>, is independent of temperature. The parameters determined for carbon dioxide are listed in Table 1, together with linalool. The critical temperature for carbon dioxide estimated by the parameters in Table 1 is 309.0 K, which is close to the experimental value (304.2 K).

Furthermore, we attempted to adopt the parameters determined for carbon dioxide for the VLE for the carbon dioxide + linalool system to other binary systems. Several binary systems : carbon dioxide + decane (nonpolar), carbon dioxide + benzene (nonpolar), carbon dioxide + methanol (polar), and carbon dioxide + ethanol (polar) were examined. The correlation effectivenesses are given in Table 2.

### Conclusion

The vapor-liquid equilibria for carbon dioxide + high-boiling component systems were correlated by using the SPHCT. The parameters of high-boiling components can be calculated from the linear functions of *ECN*. The parameters for carbon dioxide were determined to fit the experimental VLE for the carbon dioxide + linalool system at 323.2 K. Using these parameters, the VLE for carbon dioxide + high-boiling component systems are correlated well.

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### Nomenclature

<i>c</i>	= number of external degrees of freedom	[-]
<i>ECN</i>	= effective carbon number	[-]
<i>k</i>	= Boltzmann constant	[J·K <sup>-1</sup> ]
<i>k</i> <sub><i>ij</i></sub>	= binary interaction parameter	[-]
<i>N</i>	= number of data	[-]
<i>p</i>	= total pressure	[Pa]
<i>p</i> <sup>hc</sup>	= hard chain pressure term	[Pa]
<i>R</i>	= gas constant	[Pa·m <sup>3</sup> ·K <sup>-1</sup> ·mol <sup>-1</sup> ]
<i>T</i>	= temperature	[K]
<i>T</i> <sub>b</sub>	= normal boiling point	[K]
<i>v</i>	= molar volume	[m <sup>3</sup> ·mol <sup>-1</sup> ]
<i>v</i> <sup>*</sup>	= close-packed volume	[m <sup>3</sup> ·mol <sup>-1</sup> ]
<i>x</i>	= mole fraction in liquid phase	[-]
<i>y</i>	= mole fraction in vapor phase	[-]
<i>Z</i> <sub>M</sub>	= maximum coordination number	[-]
$\epsilon$	= interaction energy parameter	[J·mol <sup>-1</sup> ]
$\xi$	= parameter in Eqn. (3)	[-]
<Subscripts>		
1	= carbon dioxide	
2	= high-boiling component	
calc	= calculated value	
exp	= experimental value	
<i>i, j</i>	= components <i>i</i> and <i>j</i>	

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