SHORT COMMUNICATION

Measurement and Correlation of Vapor-Liquid Equilibria of the Binary Carbon Dioxide-Chloroform Mixture System

Jihoon Im, Hun Yong Shin* and Hwayong Kim[†]

School of Chemical Engineering & Institute of Chemical Processes, Seoul National University,
Shinlim-dong, Gwanak-gu, Seoul 151-744, Korea
*Department of Chemical Engineering, Seoul National University of Technology,
Kongneung-2 Dong, Nowon-Gu, Seoul 139-743, Korea
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Abstract−Binary vapor liquid equilibrium data of the carbon dioxide+chloroform system were measured at five isotherms from 310.13 K to 333.32 K. A circulating type apparatus with on-line gas chromatography was used in this study. The experimental data were correlated by classical Peng-Robinson equation of state using van der Waals one fluid mixing rules and the multi-fluid nonrandom lattice fluid (MF-NLF) equation of state.

Key words: Vapor-Liquid Equilibria, Carbon Dioxide, Chloroform, Equation of State

INTRODUCTION

Production of micro or submicro size particles using supercritical fluid technologies such as rapid expansion of supercritical solutions (RESS) and supercritical antisolvent (SAS) process is of interest in various fields of polymer and pharmaceutical industries. Those techniques are effective and promising methods to make fine particles [Reverchon et al., 1999, 2000; Jung et al., 2001]. As a supercritical fluid, carbon dioxide (CO_2) is frequently used, because of its special characteristics in its supercritical condition and environmentally benign properties. CO_2 has liquid-like density in the supercritical states and viscosity of supercritical CO_2 (Sc-CO_2) is lower than that of the liquefied CO_2. Those processes using Sc-CO_2 are also operated at mild conditions, because it has low critical temperature; further, it is nontoxic, nonflammable and cheap. Chloroform is generally a good solvent for polymers such as poly(L-lactic acid) (L-PLA), poly(vinyl pyrrolidone) (PVP), poly(methyl methacrylate) (PMMA), etc. Thus, chloroform is often used for various particle formation processes as a solvent [Jung et al., 2001; Sakari et al., 2000].

Thermodynamic knowledge of the supercritical solutions, especially information about phase behavior, is very important, because the knowledge is one of the basics for modeling the processes. The calculation of the nucleation rate, diffusion rate and supersaturation is essential to study particle formation, but in order to calculate those, the phase behavior of the supercritical solutions must be known [Türk et al., 2000; Werling et al., 1999, 2000]. Moreover, to design the processes and to find optimum operating conditions to control the particle size, information of the phase behavior is also needed. Therefore, we measured binary vapor liquid equilibrium data of the CO_2+ chloroform system at temperature from 310.13 K to 333.32 K. The measured data were correlated by the multi-fluid nonrandom lattice fluid (MF-NLF) equation of state based on a rigorous approxima-

tion of the nonrandom lattice-hole theory proposed by Guggenheim [1952]. We also calculated the system by using the Peng-Robinson equation of state (PR-EOS) with van der Waals one fluid mixing rules to compare the results.

EXPERIMENTS

1. Materials

CO_2 of 99.99% purity was supplied by Korean industrial gases. Chloroform of minimum 99.9% (HPLC grade) purity was supplied by Aldrich. Both components were used without further purification in these experiments.

2. Apparatus

Details of this apparatus are given in our previous studies [Im et al., 2004]. An equilibrium cell was made of 316 stainless-steel, and its internal volume was approximately 320 ml. CO_2 and chloroform were introduced into this cell, and reached vapor-liquid equilibrium. The cell had two reinforced glass windows of 19 mm thickness on both sides of the cell, through which the phase boundary could be observed. We used a gas booster pump for charging CO_2 into the cell, and a liquid pump for a solvent. Two magnetic pumps were used to circulate the vapor and liquid phases. By circulating the vapor and liquid phases with two magnetic pumps, equilibrium state was quickly attained. In our experience, equilibrium was reached about an hour. The temperature of the system was monitored by the model 5627 by Hart Scientific Co. with accuracy of 0.05 °C, and the pressure by the model Super TJE by Sensotec Co. with accuracy of 0.05 bar. We used a gas chromatograph to analyze the vapor and liquid phase compositions. A packed column with OV17 packing material (length, 6 m; mesh size, 80/100; 1/8 inch stainless steel; from Restek) was used.

3. Experimental Procedure

At first, the cell was evacuated by a vacuum pump. Chloroform was injected into the cell, and then CO_2 was charged. Two magnetic pumps were started to circulate vapor and liquid phases. When equilibrium was reached, the vapor and liquid samples were taken

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[†]To whom correspondence should be addressed.
E-mail: hwayongk@snu.ac.kr

into the on-line gas chromatograph to measure vapor and liquid compositions.

THERMODYNAMIC MODELS

1. Peng-Robinson Equation of State

Peng-Robinson equation of state [Peng et al., 1976] is as follows.

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \tag{1}$$

$$a(T) = \left(0.45724\frac{R^2T_c^2}{P_c}\right)\alpha(T) \tag{2}$$

$$b(T_c) = 0.07780\frac{RT_c}{P_c} \tag{3}$$

$$\alpha(T) = \left[1 + \kappa\left(1 - \sqrt{\frac{T}{T_c}}\right)\right]^2 \tag{4}$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{5}$$

where T_c and P_c are the critical temperature and the critical pressure of the pure substance, respectively, and ω is the acentric factor. These parameters are summarized in Table 1. The van der Waals one fluid mixing rules used in this study are given by

$$a_m = \sum_i\sum_j x_i x_j a_{ij} \tag{6}$$

$$b_m = \sum_i x_i b_i \tag{7}$$

$$a_{ij} = \sqrt{a_i a_j}(1-k_{ij}) \tag{8}$$

where k_{ij} is the binary interaction parameter. Only one binary interaction parameter was used in this study. It was used to regress the experimental vapor liquid equilibrium data. The subscript m denotes mixture.

2. MF-NLF

The general expression of the MF-NLF model [Shin et al., 2001] can be written as

$$P = \frac{1}{\beta V_H}\left\{\frac{z}{2}\ln\left[1+\left(\frac{q_M}{r_M}-1\right)\rho\right] - \ln(1-\rho) + \frac{z}{2}\sum_{i=1}^c\theta_i\left(\frac{\tau_{0i}}{\sum_{k=0}^c\theta_k\tau_{ki}}-1\right)\right\} \tag{9}$$

where $q_M = \sum x_i q_i$, $r_M = \sum x_i r_i$, $r_i = V^*/V_H$, $\rho = \sum\rho_i$ and $\rho_i = N_i r_i/N_r = V^*/V$.

We set the unit lattice cell volume (V_H) as 9.75 cm^{3}mol^{-1} and the coordination number (z) as 10. The molecular size parameters (V^*) were determined by using the pure critical properties. The molecular energy parameters were determined by regressing the experimen-

Table 1. Physical properties

	CO$_2$	CHCl$_3$
T_c/K	304.12[a]	536.50[a]
P_c/bar	73.74[a]	55.00[a]
ω	0.225[a]	0.218[b]

[a]The properties of Gases and Liquids.
[b]Chemical Engineering Research Information Center

Table 2. Coefficients of molecular parameters for the MF-NLF EOS

Chemicals	E_a(K)	E_b	E_c(K^{-1})	V^*(cm^{3}mol^{-1})
CO$_2$	110.8498	−0.1674	1.5283e-4	43.0286
CHCl$_3$	124.0032	−0.0893	1.3065e-4	84.1064

tal vapor pressure data of the pure components and expressed as follows.

$$\varepsilon_{ii}/k = E_a + E_b T + E_c T^2 \tag{10}$$

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}(1-k_{ij}) \tag{11}$$

where k_{ij} is the binary interaction parameter. The molecular size parameters and the coefficients of Eq. (10) are listed in Table 2.

RESULTS AND DISCUSSION

The experimental vapor liquid equilibrium data of the binary CO$_2$+chloroform system at 310.13 K, 314.61 K, 321.43 K, 327.43 K and 333.32 K were obtained in this study. Fig. 1 displays the experimental data of Scurto [Scurto et al., 2001] at 333.15 K compared to our experimental data at 333.32 K. Good agreement is shown with the experimental data of Scurto. The experimental data of this study are given in Table 3. Fig. 2 also shows the experimental results. As can be seen in Fig. 2, the solubility of chloroform in CO$_2$ increases with increasing temperature and decreasing pressure. The experimental data were correlated with the PR-EOS and the MF-NLF EOS, and the simplex algorithm was used to determine the binary interaction parameter (k_{ij}) of both equations of state. Only one binary interaction parameter was used for both equations of sate in this study. The objective function (OF) used in the regression is as follows.

$$OF = \sum_i^N\left|\frac{P_{exp}-P_{cal}}{P_{exp}}\right| \tag{12}$$

where N is the number of experimental data points and P_{exp} and P_{cal} are the experimental and the calculated pressures, respectively. The binary interaction parameters for the CO$_2$+chloroform system and
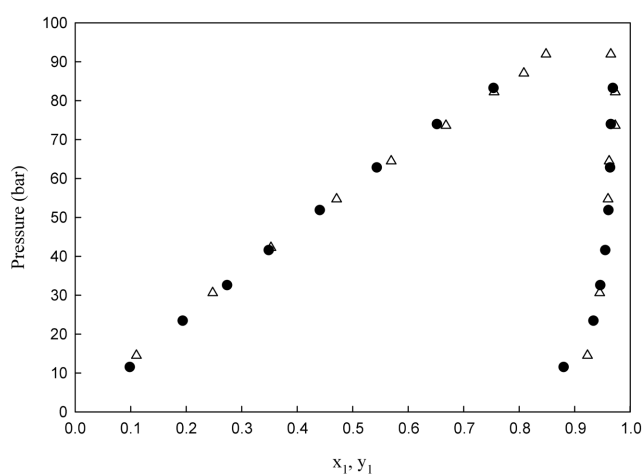
Fig. 1. Experimental vapor-liquid equilibrium data of the CO$_2$ (1)+chloroform (2) system at 333.32 K compared to the data of Scurto et al. at 333.15 K: ●, this study; △, Scurto et al.

Table 3. Measured vapor-liquid equilibrium data of the CO$_2$ (1)+ chloroform (2) system

P(bar)	x$_1$	P(bar)	y$_1$	P(bar)	x$_1$	y$_1$
T=310.13 K				T=314.61 K		
9.05	0.1126	6.57	0.9279	9.68	0.1059	0.9214
19.26	0.2343	13.18	0.9648	18.94	0.2047	0.9526
29.18	0.3617	20.84	0.9745	27.88	0.3007	0.9680
36.77	0.4566	28.17	0.9800	36.47	0.4052	0.9745
45.54	0.5807	37.65	0.9836	44.52	0.4960	0.9771
55.90	0.7236	45.54	0.9852	56.53	0.6605	0.9797
71.67	0.9016	55.90	0.9865	65.81	0.7917	0.9813
		71.67	0.9897	71.14	0.8535	0.9821

P(bar)	x$_1$	y$_1$	P(bar)	x$_1$	y$_1$	P(bar)	x$_1$	y$_1$
T=321.43 K			T=327.43 K			T=333.32 K		
10.88	0.1072	0.9122	10.72	0.0989	0.8970	11.54	0.0984	0.8803
21.93	0.2119	0.9526	20.58	0.1850	0.9406	23.42	0.1938	0.9339
30.42	0.2979	0.9635	30.63	0.2755	0.9562	32.60	0.2739	0.9462
39.33	0.3896	0.9691	39.63	0.3608	0.9627	41.55	0.3486	0.9550
47.63	0.4792	0.9724	47.53	0.4371	0.9665	51.87	0.4408	0.9608
56.70	0.5839	0.9743	55.49	0.5199	0.9687	62.78	0.5435	0.9639
65.48	0.6913	0.9755	67.39	0.6442	0.9699	73.94	0.6517	0.9652
74.17	0.7962	0.9768	78.17	0.7631	0.9697	83.22	0.7538	0.9687
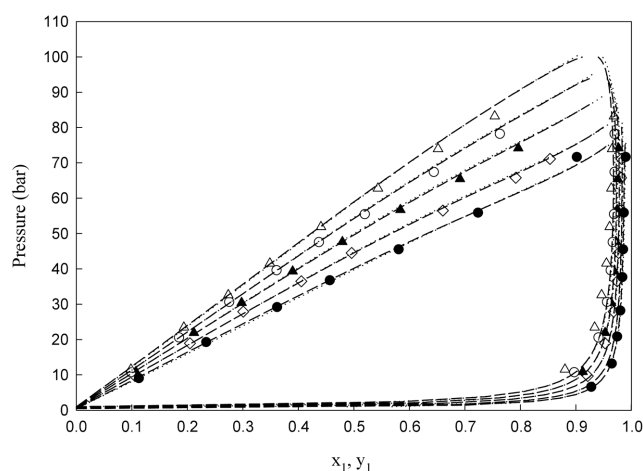
Fig. 2. Experimental vapor-liquid equilibrium data of the CO$_2$ (1) +chloroform (2) system and performance of the calculated results : △, 333.32 K; ○, 327.43 K; ▲, 321.43 K; ◇, 314.61 K; ●, 310.13 K; —, PR-EOS with k$_{ij}$=0.0486; ··, MF-NLF EOS with k$_{ij}$=0.0255.

Table 4. Interaction parameter and AAD (%) for the CO$_2$+chloroform systems

T (K)	EOS	k$_{ij}$	AADP (%)
310.13	PR	0.0408	1.2
	MF-NLF	0.0211	1.4
314.61	PR	0.0497	1.1
	MF-NLF	0.0286	1.3
321.43	PR	0.0503	1.3
	MF-NLF	0.0267	1.6
327.43	PR	0.0485	1.5
	MF-NLF	0.0263	1.7
333.32	PR	0.0479	1.6
	MF-NLF	0.0255	2.5
overall	PR	0.0486	1.4
	MF-NLF	0.0255	1.8

$$\text{AAD } (\%) = (100/N)\sum_i^N |P_{i(exp)} - P_{i(cal)}|/P_{i(exp)}$$

the absolute average deviation of pressure (AADP) are summarized in Table 4, and the performance of the PR-EOS and the MF-NLF EOS is illustrated in Fig. 2. Although slightly overestimating the pressure as approaching near critical region of the mixture, both equations of state fit well with the experimental data in that overall AADP of the PR-EOS is 1.4% and that of the MF-NLF EOS is 1.8%. Though the calculated results of the PR-EOS are relatively better than those of the MF-NLF EOS, the MF-NLF EOS seems more practicable than the PR-EOS in the target systems of this study, such as SAS and RESS, because the MF-NLF EOS can be applied to predict the phase behavior of the supercritical fluid system containing polymers [Shin et al., 1998; Jung et al., 2002], but predicting the system

containing polymers by using the PR-EOS is difficult. It is supposed that the calculation of the phase equilibria by using the MF-NLF EOS is suitable for the prediction of the phase behavior for a system containing polymers.

CONCLUSION

We measured the vapor-liquid equilibrium data for the CO$_2$+chloroform system with a circulation type apparatus. The measured data were correlated by the MF-NLF EOS and PR- EOS using van der Waals one fluid mixing rules. Good correlation results were obtained by using both equations of state and especially, the MF-NLF EOS is useful in the fields of producing fine polymer powders, because it is expected that the EOS has good performance to predict the phase

behavior of the system containing polymers.

REFERENCES

Chemical Engineering Research Information Center Home Page, http://www.cheric.org.

Guggenheim, E. A., *Mixtures*, Clarendon Oxford (1952).

Im, J., Bae, W., Lee, J. and Kim, H., "Vapor-Liquid Equilibria of Binary Carbon Dioxide-Tetrahydrofuran Mixture System," *J. Chem. Eng. Data*, **49**, 35 (2004).

Jung, J. K., Joung, S. N., Shin, H. Y., Kim, S. Y., Yoo, K.-P., Huh, W. and Lee, C. S., "Measurements and Correlation of Hydrogen-bonding Vapor Sorption Equilibrium Data of Binary Polymer Solutions," *Korean J. Chem. Eng.*, **19**, 296 (2002).

Jung, J. and Perrut, M., "Particle Design Using Supercritical Fluids: Literature and Patent Survey," *J. Supercrit. Fluids*, **20**, 179 (2001).

Peng, D. and Robinson, D. B., "New Two-Constant Equation of State," *Ind. Eng. Chem. Fundam.*, **15**, 59 (1976).

Poling, B. E., Prausnitz, J. M. and O'Connel, J. P., *The Properties of Gases and Liquids*, 5th edition, McGraw-Hill: New York (2001).

Reverchon, E., Dolla Porta, G and Falivene, M. G, "Process Parameters and Morphology in Amoxicillin Micro and Submicro Particles Generation by Supercritical Antisolvent Precipitation," *J. Supercrit. Fluids*, **17**, 239 (2000).

Reverchon, E., "Supercritical Antisolvent Precipitation of Micro- and Nano-Particles," *J. Supercrit. Fluids*, **15**, 1 (1999).

Sakari, M., Darrat, I. and Knutson, B. L., "Generation of Microparticles Using CO_2 and CO_2-Philic Antisolvent," *AIChE J.*, **46**, 1850 (2000).

Scurto, A. M., Lubbers, C. M., Xu, G and Brennecke, J. F., "Experimental Measurement and Modeling of the Vapor-liquid Equilibrium of Carbon Dioxide+Chloroform," *Fluid Phase Equilib.*, **190**, 135 (2001).

Shin, H. Y., Haruki, M., Yoo, K.-P., Iwai, Y. and Arai, Y., "Phase Behavior of Water+Hydrocarbon Binary Systems by Using Multi-fluid Nonrandom Lattice Hydrogen Bonding Theory," *Fluid Phase Equilib.*, **189**, 46 (2001).

Shin, H. Y., Yoo, K.-P., Lee, C. S., Tamura, K. and Arai, Y., "Rigorous and Simplified Lattice-hole Equations of State for Calculating Specific Volumes of Common Pure Polymers," *Korean J. Chem. Eng.*, **15**, 15 (1998).

Türk, M., "Influence of Thermodynamic Behaviour and Solute Properties on Homogeneous Nucleation in Supercritical Solutions," *J. Supercrit. Fluids*, **18**, 169 (2000).

Werling, J. O. and Debenedetti, P. G, "Numerical Modeling of Mass Transfer in the Supercritical Antisolvent Process," *J. Supercrit. Fluids*, **16**, 167 (1999).

Werling, J. O. and Debenedetti, P. G, "Numerical Modeling of Mass Transfer in the Supercritical Antisolvent Process: Miscible Conditions," *J. Supercrit. Fluids*, **18**, 11 (2000).