CO_2+chloroform 이성분계의 기액상평형

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High-pressure Vapor Liquid Equilibria of Binary CO_2-chloroform System

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INTRODUCTION

We are especially interested in $scCO_2$ and solvent systems because these data are required not only to predict the $scCO_2$-solvent mixture but also to be used for the SAS(Supercritical Antisolvent process). SAS is a useful process to obtain micronized particles which can be used in various fields of polymer, biopolymer, pharmaceutical industries, etc. This method is based on the following principle. When the solution is injected into antisolvent, which is miscible with the solvent, but can not dissolve the solute, the solute is supersaturated and precipitated. At this time, the formation of micronized particles is occurred.[1,2] The important thing considered in SAS is the choice of the solvent and the antisolvent. They must be completely miscible with each other at operating condition and the antisolvent must not dissolve the solute. CO_2 is generally used as an antisolvent because not only is it miscible with various solvents, but it also has low critical temperature. Moreover, it is nontoxic, nonflammable and cheap. To choose a possible solvent for the CO_2, various vapor liquid equilibrium data of CO_2 and solvents are required, but they are scarce. Therefore, we measured binary vapor liquid equilibria of CO_2- chloroform. We used the circulation method for the experiments. The measured data were correlated by Peng-Robinson equation of state(EOS) using van der Waals one fluid mixing rule.

EXPERIMENTAL

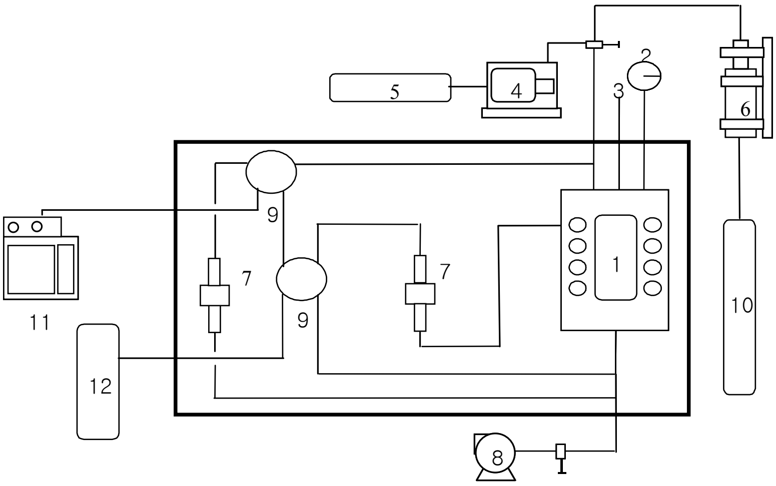
Chemicals

CO_2 of 99.99% purity was supplied by Korean industrial gases. chloroform of minimum 99.9% (HPLC grade) purity was supplied by J.T. Baker.

Apparatus

Figure 1. shows the schematic diagram of the experimental apparatus. This apparatus was designed to measure vapor-liquid equilibrium data. The main components of the apparatus consisted of 5 parts. An equilibrium cell was made of 316 stainless-steel, and its internal volume was approximately 320ml. CO_2 and a solvent were first introduced into this cell, and reached vapor-liquid equilibrium. The cell had two reinforced glass windows of 19mm 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 phase. By circulating the

vapor and liquid phase with two magnetic pumps, the equilibrium state was quickly attained. The temperature of the system was monitored by the model 5627 by Hart Scientific Co. with accuracy of 0.05℃, and the pressure by the model Super TJE by Sensotec Co. with accuracy of 0.05%. We used a gas chromatograph to analyze the vapor and liquid phase composition. A packed column with OV17 packing material was used.



1. Cell
2. Pressure gauge
3. Thermocouple
4. Liquid pump
5. Sample cylinder
6. Buster pump
7. Magnetic pump
8. Vacuum pump
9. Sampling valve
10. CO_2 tank
11. GC
12. Carrier gas

Figure 1 . Experimental apparatus

Experimental Procedure

After the cell was evacuated, a solvent was injected into the cell, and then CO_2 was charged. Two magnetic pumps were started, and vapor and liquid phases were circulated. When the equilibrium was reached, the vapor and liquid samples were taken into the gas chromatograph to measure vapor and liquid composition.

RESULT AND DISCUSSION

We choose the CO_2-toluene binary system at 311.26K by Ng et al.[3] to test the validity of our new experimental apparatus and good results were obtained. Figure. 2 shows CO_2-toluene vapor liquid equilibrium data of Ng et al. at 311.26K compared to our data. As Figure 2. shows, the experimental data at 311.26K agree well with the compared data.

Vapor liquid equilibrium data were measured for CO_2-chloroform at 310.13, 314.78, 321.43 and 327.43K.

Experimental data were correlated with Peng-Robinson equation of state[4] using van der Waals one fluid mixing rule.

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

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

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

$$a_m = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}(1-k_{ij}) \tag{4}$$

$$b_m = \sum_i x_i b_i \tag{5}$$

Physical properties of each component are listed in Table 1.

Table 1. Physical properties

	CO_2	$CHCl_3$
Tc/K	304.12[5]	536.50[5]
Pc/bar	73.74[5]	55.00[5]
ω	0.225[5]	0.218[6]

The binary interaction parameter(k_{ij}) was obtained by regressing the experimental vapor liquid equilibrium data, by minimizing the objective function(OBF). We used the Marquardt algorithm to minimize the objective function which is as follows.

$$OBF = \sum_i \left| \frac{P_{\exp} - P_{cal}}{P_{\exp}} \right| \tag{6}$$

Table 2. shows the binary interaction parameters for the CO_2+chloroform system. The agreement is satisfactory with the absolute average deviation less than 1.71% for CO_2+chloroform. Vapor liquid equilibrium data for the CO_2+chloroform system are represented graphically and compared with results of calculations in Figure 3.

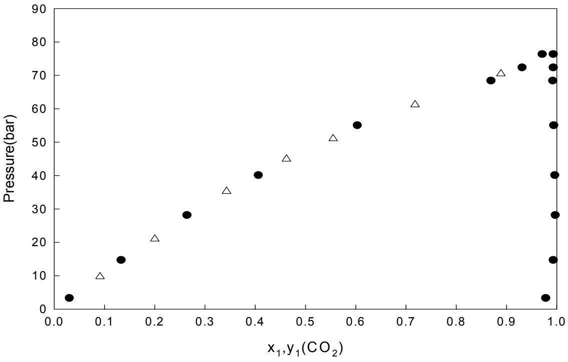


Figure 2. Experimental data at 311.26K (this study : △) compared to data of Ng et al. (●)

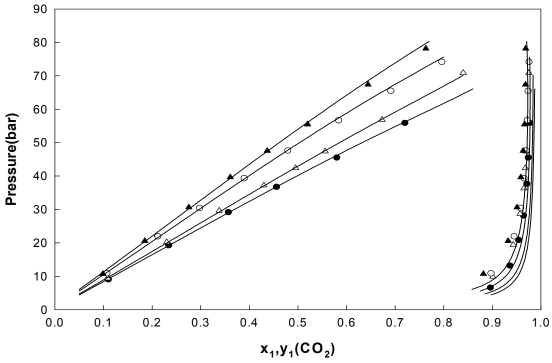


Figure 3. Vapor-liquid equilibria of the CO_2+chloroform system : (●) experimental data at 310.13K : (△) 314.78K : (○) 321.43K : (▲) 327.43K

Table 2. Interaction parameter and AAD(%)

system	T/K	k_{12}	AAD(%)
CO_2+$CHCl_3$	310.13	0.0408	1.24
	314.78	0.0376	0.89
	321.43	0.0494	1.61
	327.43	0.0476	1.71

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

CONCLUSION

We measured vapor-liquid equilibrium data for CO_2+chloroform. We used a circulation type apparatus for the experiments. The measured data were correlated well by Peng-Robinson EOS using van der Waals one fluid mixing rule with one adjustable parameter.

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