열물성연구회 세미나

초임계 이산화 탄소 및 고분자합성을 위한 모노머의 상평형 연구

2. 불소계 모노머와 초임계 이산화탄소의 상평형

2003년 10월 13일

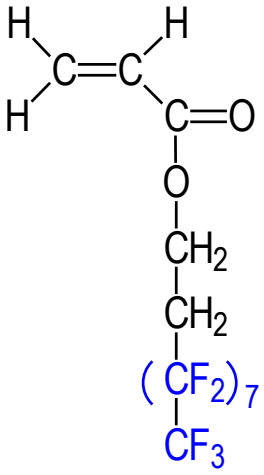
서울대학교 응용화학부 열물성연구실

신현순, 배 원, 김화용

Thermophysical Properties Lab.

Materials

HDFDA



[27905-45-9]

(min. 97%)

From **Aldrich**

Carbon dioxide

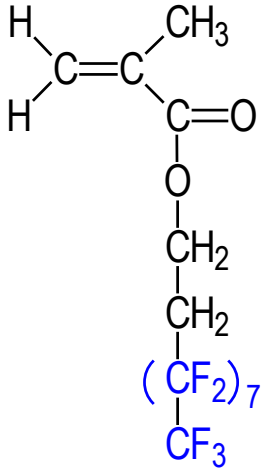
O=C=O

[124-38-9]

(min. 99.99%)

From Korea Industrial Gases

HDFDMA

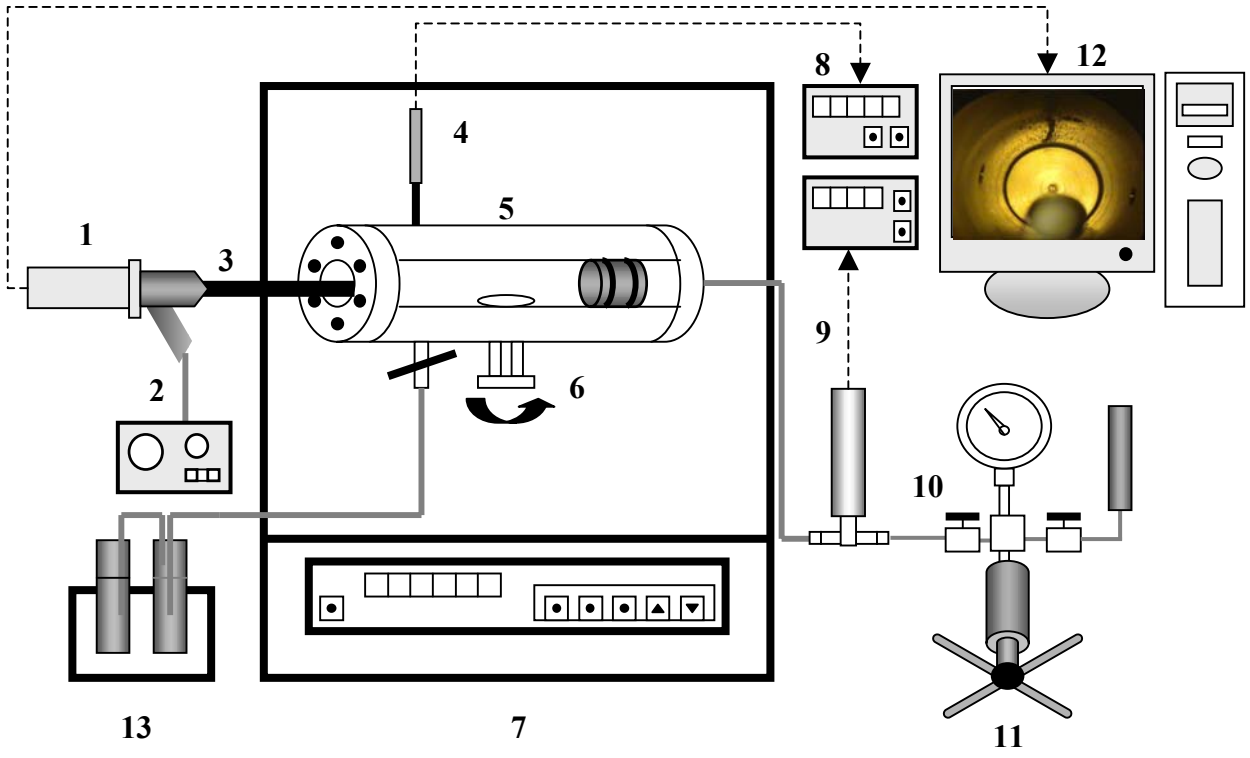


[1996-88-9]

(min. 97%)

From **Aldrich**

Experimental Apparatus



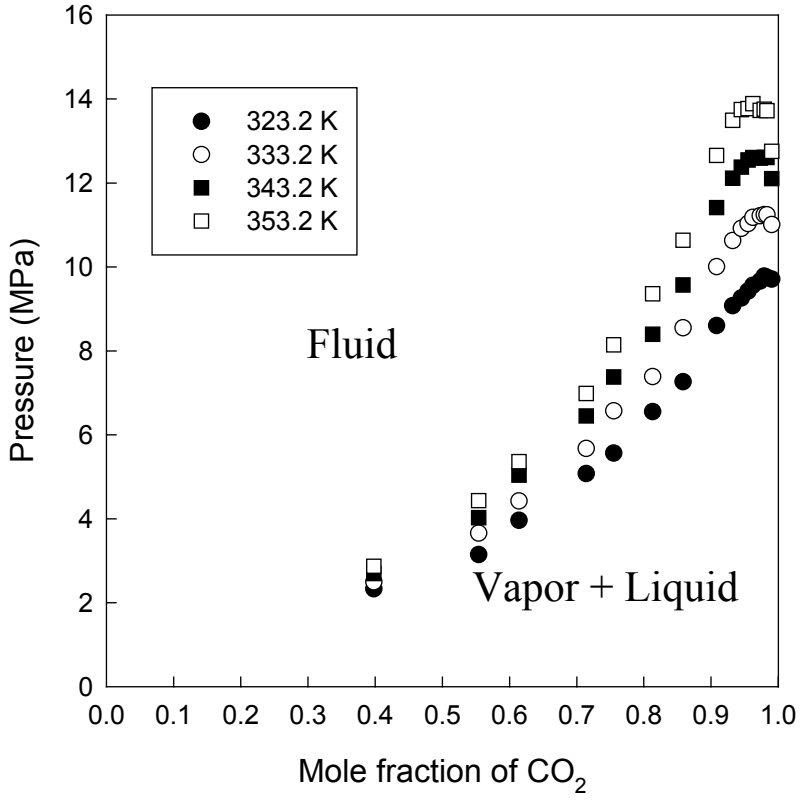
1. Camera
2. Light source
3. Borescope
4. Thermocouple
5. View cell
6. Magnetic stirrer
7. Air bath
8. Digital thermometer
9. Digital pressure transducer
10. Pressure gauge
11. Hand pump
12. Computer monitor
13. Trap

Figure 1. Schematic Diagram of the experimental apparatus

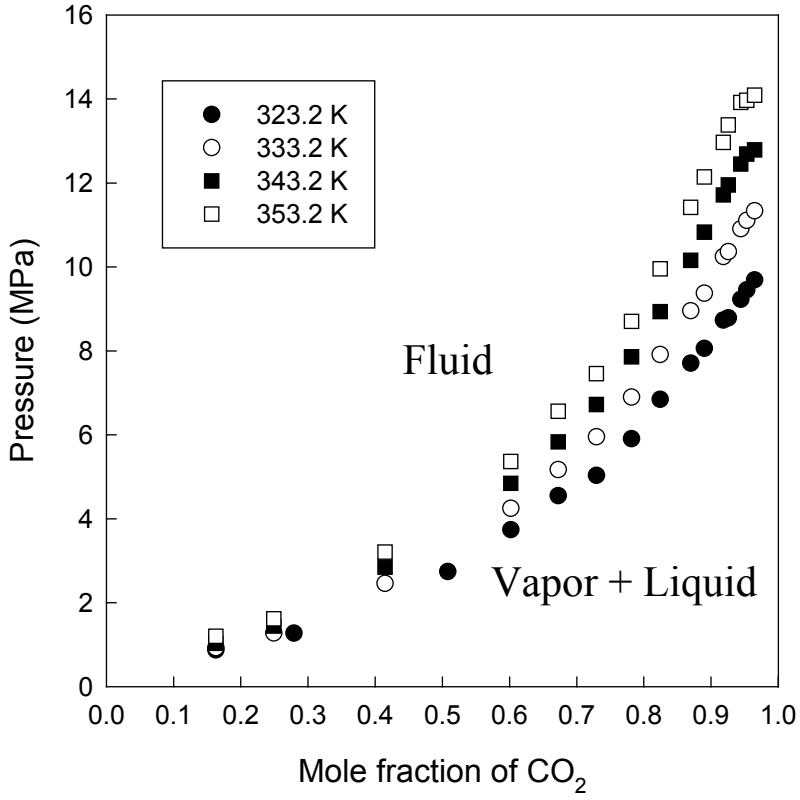
Experimental Apparatus

- **Temperature measurement**
  - Thermometer
    - ✓ Fast response PRT
    - ✓ Hart Scientific INC., model 5622-32SR
    - ✓ Accuracy of ±0.045 K
  - Indicator
    - ✓ Hart Scientific INC., model 1502
- **Pressure measurement**
  - Digital pressure transducer
    - ✓ Paroscientific INC., model 43KR-HHT-101
    - ✓ Accurate to 0.01% of reading
  - Indicator
    - ✓ Paroscientific INC., model NO.730

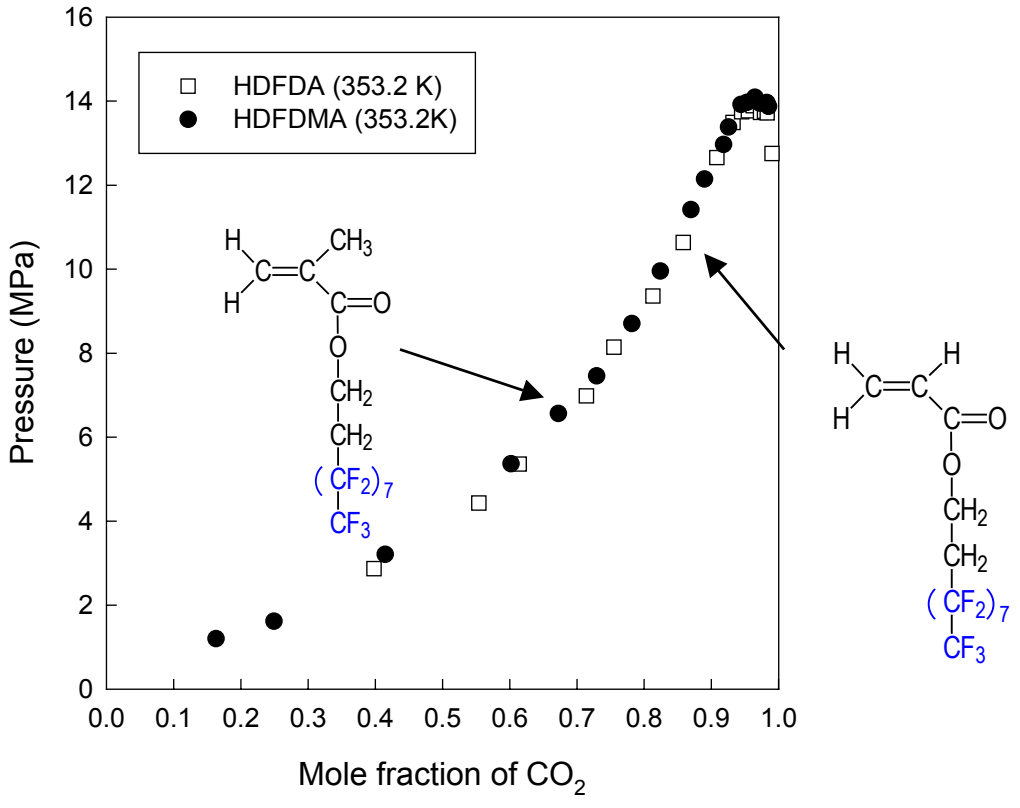
Experimental Result : CO_2-HDFDA system



Experimental Result : CO_2-HDFDMA system



Fluoro acrylate and methacrylate



Correlation of CO_2-fluoro monomer System

- Peng – Robinson Equation of State [1]

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

- van der Waals 1-fluid mixing rule

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \qquad b_m = \sum_i \sum_j x_i x_j b_{ij}$$

$$a_{ij} = \sqrt{a_{ii} a_{jj}}\,(1 - k_{ij}) \qquad b_{ij} = \frac{(b_{ii} + b_{jj})}{2}(1 - \eta_{ij})$$

Two adjustable parameters !

Correlation of CO_2-fluoro monomer System

- Object function(OBF)

$$OBF = \sum_{i}^{N} \left(\frac{P_{\exp} - P_{cal}}{P_{\exp}} \right)^2$$

- Root Mean Squared relative Deviation(RMSD)

$$RMSD\ (\%) = \sqrt{\frac{OBF}{ND}} * 100$$

- Optimization Algorithm

Marquardt algorithm [2]

Critical constants and acentric factors

- Estimated with Joback method [5]

$$T_b(K) = 198.2 + \sum n_i \Delta_{bi}$$

$$T_c(K) = T_b\left[0.584 + 0.9651\left(\sum n_i \Delta_T\right) - \left(\sum n_i \Delta_T\right)^2\right]^{-1}$$

$$P_c(bar) = \left[0.113 + 0.0032 N_{atoms} - \sum n_i \Delta_P\right]^{-2}$$

- Estimated with Lee-Kesler method [5]

$$\omega = \frac{\alpha}{\beta} \qquad \theta = \frac{T_b}{T_c}$$

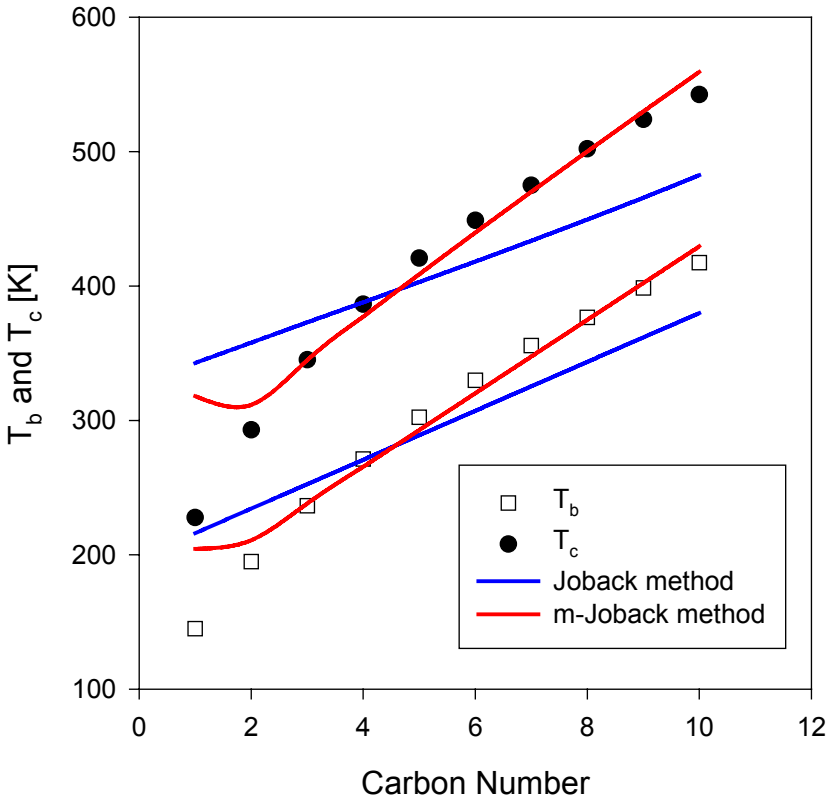
$$\alpha = -\ln P_c - 5.92714 + 6.09648\theta^{-1} + 1.28862 \ln\theta - 0.169347\theta^6$$

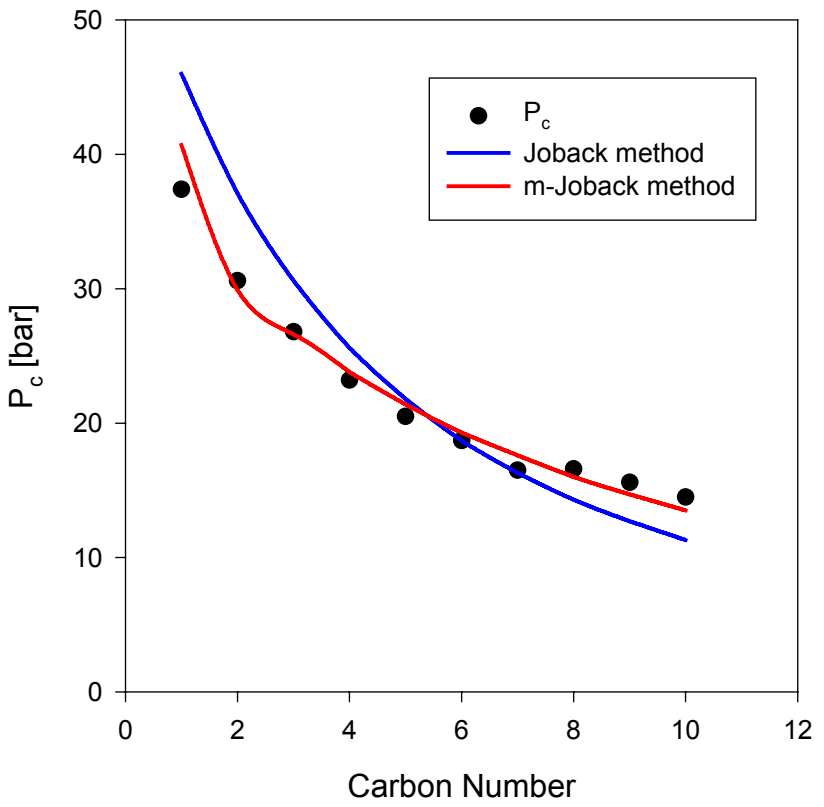
$$\beta = 15.2518 - 15.6875\theta^{-1} - 13.4721 \ln\theta + 0.43577\theta^6$$

Modified Joback Method

	T_b [K]	T_c	P_c
$-CH_3$	23.58	0.0141	-0.0012
$=CH_2$	18.18	0.0113	-0.0028
=C<	24.14	0.0117	0.0011
=CH-	24.96	0.0129	-0.0006
-COO-	81.10	0.0481	0.0005
$>CH_2$	22.88	0.0189	0.0000
>C<	18.25	0.0067	0.0043
-F	-0.03	0.0111	-0.0057
$-CF_2-$	30.08	0.0222	-0.0036
$-CF_3$	3.53	0.0498	-0.0210

Critical constants of perfluoroalkane





Critical constants and acentric factors

- Estimated with Constantinou/Gani method [6]

$$T_b = 204.359 \ln[\sum_k N_k (tb1k) + W \sum_j M_j (tb2j)]$$

$$T_c = 181.128 \ln[\sum_k N_k (tc1k) + W \sum_j M_j (tc2j)]$$

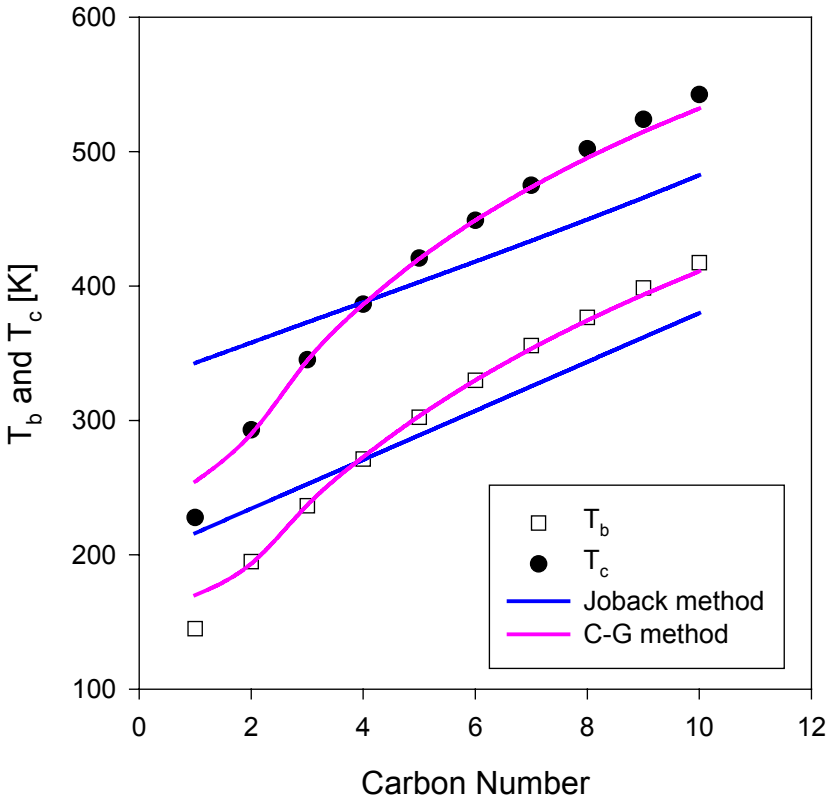
$$P_c = [\sum_k N_k (pc1k) + W \sum_j M_j (pc2j) + 0.10022]^{-2} + 1.3705$$

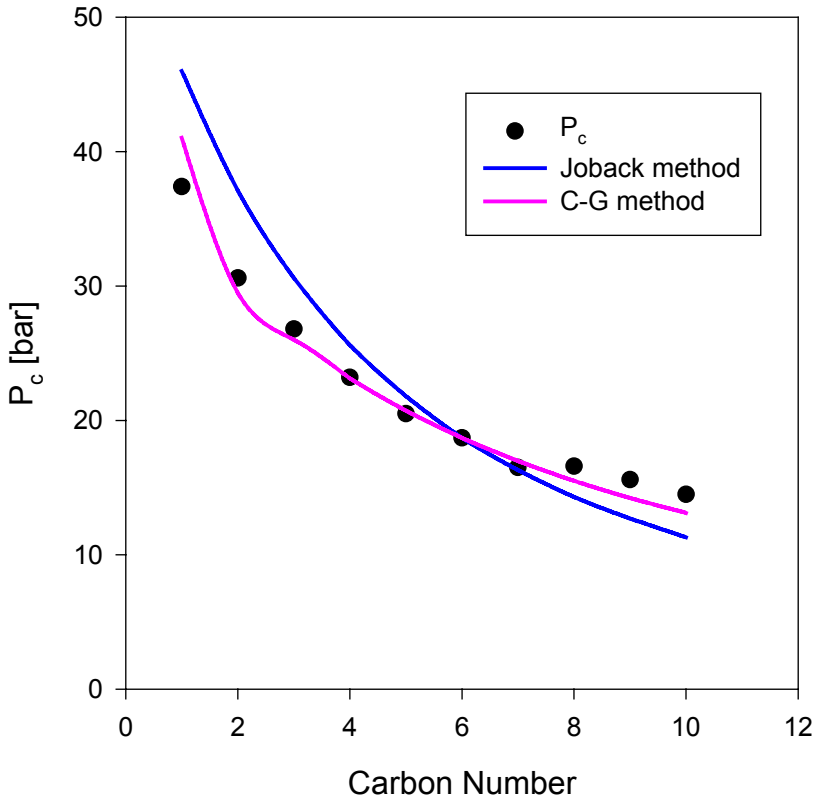
$$\omega = 0.4085\{\ln[\sum_k N_k (\omega 1k) + W \sum_j M_j (\omega 2j) + 1.1507]\}^{(1/0.5050)}$$

Constatinou / Gani method parameter

Component	T_b [K]	T_c [K]	P_c [bar]	ω
CH_2=CH(1)	1.7827	5.0146	0.0250	0.408
CH_2=C(2)	1.7117	6.5081	0.0223	0.223
CH_3(1)	0.8894	1.6781	0.0199	0.296
COO(2)	2.6446	12.1084	0.0113	**X**
CH_2 (2)	0.9225	3.4920	0.0106	0.147
CF_2 (2)	0.6115	1.7399	0.0129	**X**
CF_3 (1)	1.2880	2.4778	0.0442	**X**

Critical Constants of perfluoroalkne





Modified Joback method parameter

Component	T_c [K]	P_c [bar]	ω	Source
CO_2	304.10	73.80	0.2250	1
HDFDA	641.95	10.88	0.8167	2
	737.90	12.13	0.7702	3
	662.47	13.08	0.5870	4
HDFDMA	667.75	10.25	0.8078	2
	762.74	11.39	0.7708	3
	676.72	11.82	0.5608	4

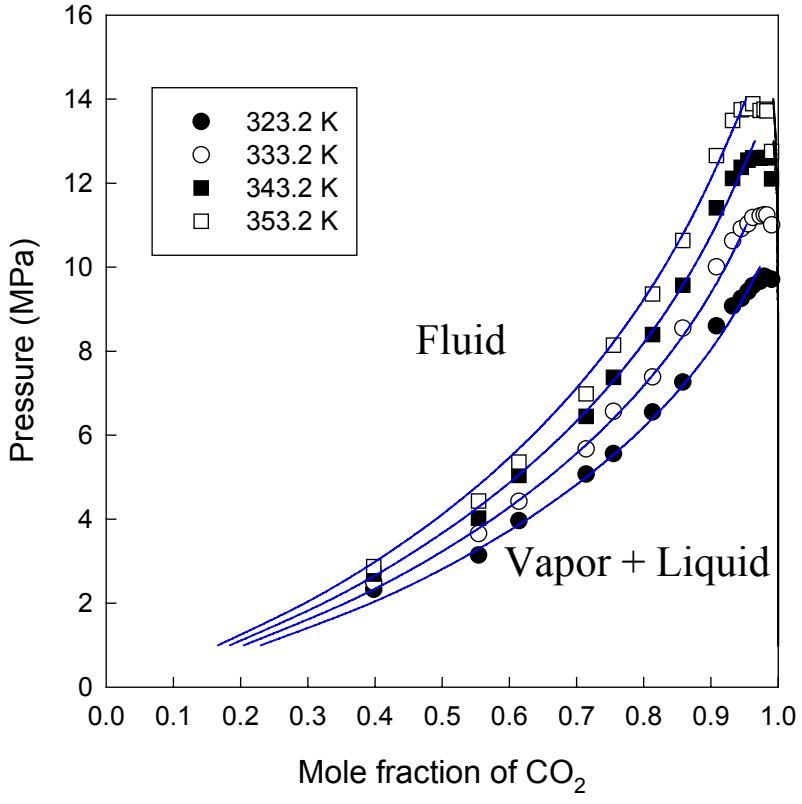
1. The Properties of Gases and liquids, 4th Ed .
2. Joback method and Lee-Kesler method
3. Modified joback method and Lee-Kesler method
4. Constantinou and Gani method and Lee-Kesler method

Result ; RMSD

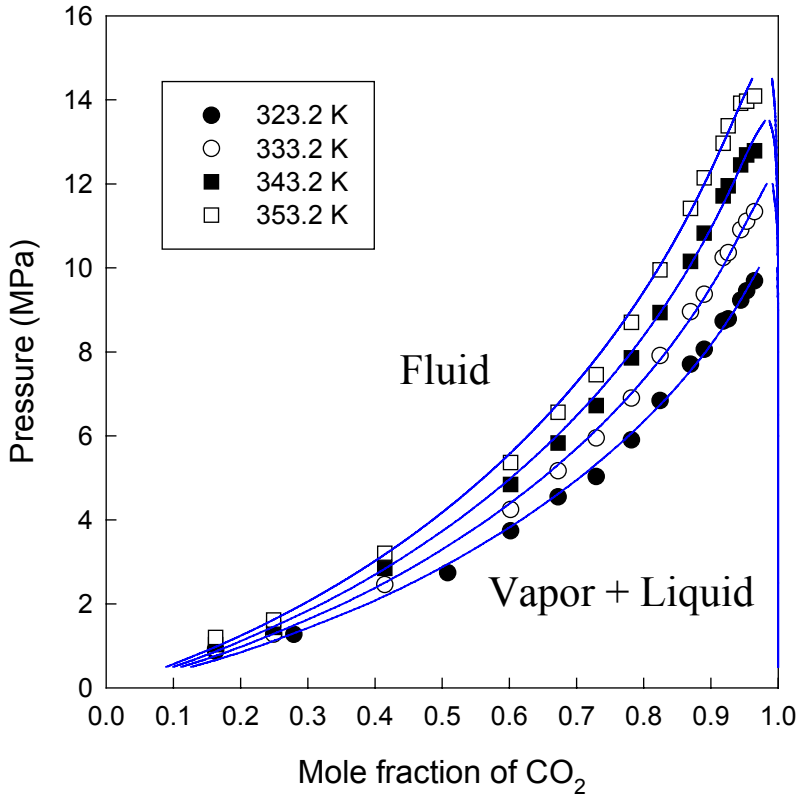
CO_2 – HDFDA system				
T(K)	k_{ij}	η_{ij}	RMSD(%)	Remark
323.2~353.2	0.0063	0.0484	3.67	Joback method
	-0.0280	0.0233	3.36	Modified Joback method
	-0.0014	0.0491	3.63	C-G method

CO_2 – HDFDMA system				
T(K)	k_{ij}	η_{ij}	RMSD(%)	Remark
323.2~353.2	0.0112	0.0428	7.17	Joback method
	-0.0180	0.0241	5.27	Modified Joback method
	0.0115	0.0460	6.88	C-G method

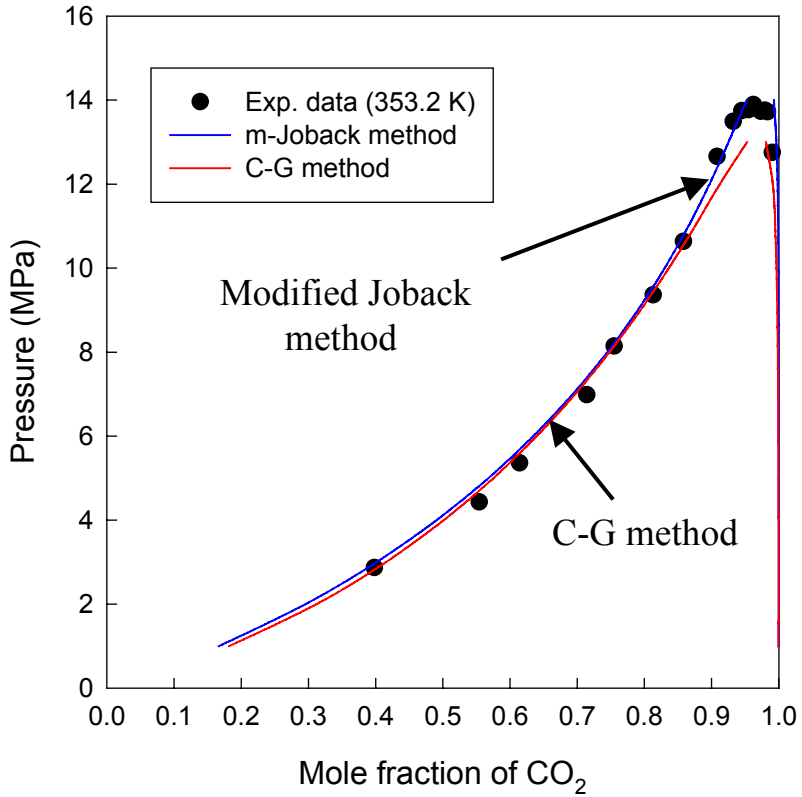
Calculation Result : CO_2-HDFDA system



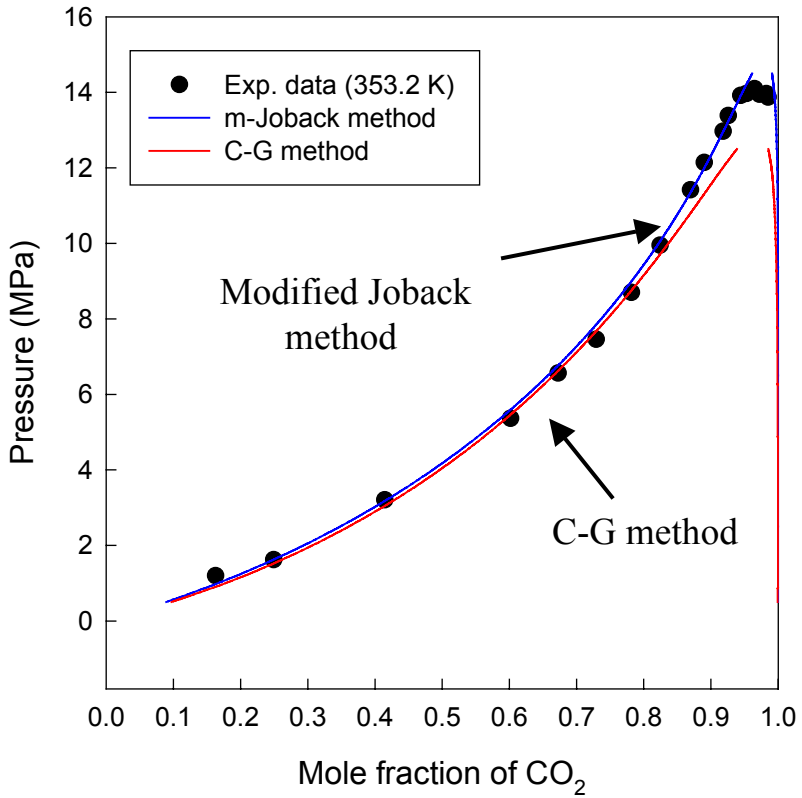
Calculation Result : CO_2-HDFDMA system



Calculation Result : CO_2-HDFDA system



Calculation Result : CO_2-HDFDMA system



Conclusion

- We measured **pressure – composition(P-x) isotherms** for binary mixture of **CO_2 + HDFDA and CO_2 + HDFDMA systems** at temperature from 323K to 353K and pressure up to 140bar.

- Good correlation result was obtained with **Peng-Robinson equation of state** with two adjustable parameters.

- Calculation result with **modified joback method** parameters for CF_3- and -CF_2- shows **overestimation** of pressure near critical region. And original **Joback method** and **Constantinou-Gani method underestimate** pressure near critical region.

- **Fluoralkyl (meth)acrylate** shows **higher solubility** in CO_2 compared with corresponding **alkyl (meth)acrylate**.

Reference

[1] D. Peng, D. B. Robinson, A new two-constant equation of state, *Ind. Eng. Chem. Fundam.* 15 (1976) 59.

[3] J. L. Kuester, J. H. Mize, Optimization techniques with Fortran, McGraw-HILL Book Company, 1973.

[4] The DIPPR Database for chemistry and materials science; Design Institute for Physical Property Data, produced by AIChE, New York, 1990.

[5] R. C. Reid, J. M. Plausnitz, Poling, B. E., The properties of Gases and liquids, 4th Ed. McGraw-HILL Book Company, 1987.

[6] L. Constantinou, R. Gani, New group contribution method for estimating properties of pure compounds, *AIChE J.*, 40 (1994) 1697.