열물성연구회 세미나

초임계 이산화 탄소 및 고분자합성을 위한 모노머의 상평형 연구

3. PVP-NVP-$scCO_2$ 계의 상평형

2003년 10월 13일

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Thermophysical Properties Lab.

Materials

Carbon dioxide

[124-38-9]

(min. 99.99%)

From Korea Industrial Gases

Ethyl Alcohol

[64-17-5]

(min. 99.9%)

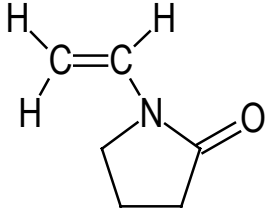
From Hayman Limited

N-vinyl pyrrolidone(NVP)

[88-12-0]

(min. 99%)

From Aldrich

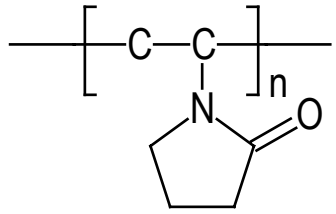


Polyvinylpyrrolidone(PVP)

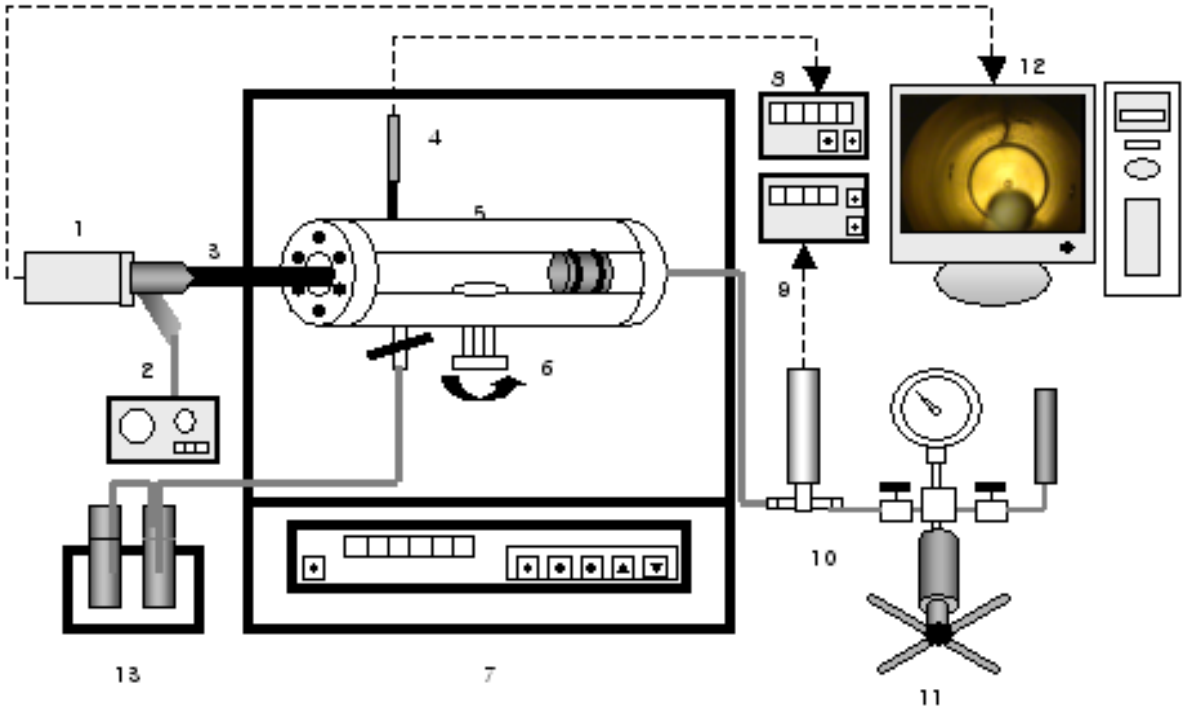
[9003-39-8]

Mw = 2,500 from Polyscience

Mw = 10,000, 29,000, 55,000 From Aldrich



Experimental Apparatus

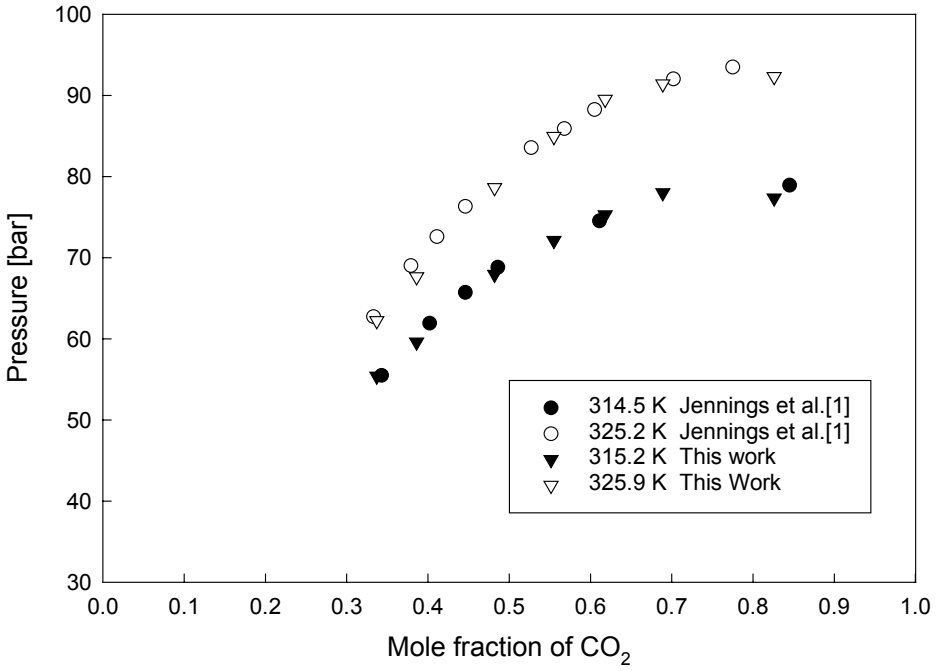


1. Camera
2. Light source
3. Borescope
4. Thermocouple
5. View cell
6. Magnetic stirrer
7. Air bath
8. Digital thermometer
9. Digital pressure transducer
10. Pressure gauge
11. Hand pump
12. Computer monitor
13. Trap

Figure 1. Schematic Diagram of the experimental apparatus

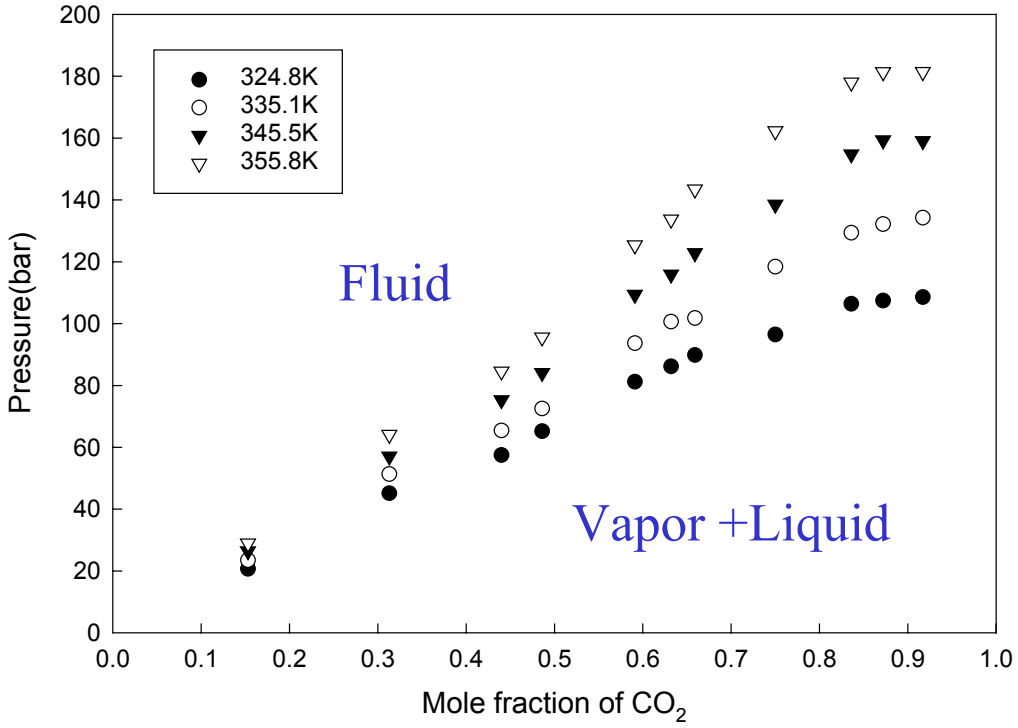
Consistency Test

Phase behavior of CO_2(1)+Ethanol(2) system



CO_2 +NVP System

Phase behavior of CO_2(1)+NVP(2) system



Correlation of CO_2-NVP System

- Peng – Robinson Equation of State [2]

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

- 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-NVP 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[3]

Critical constants and acentric factors

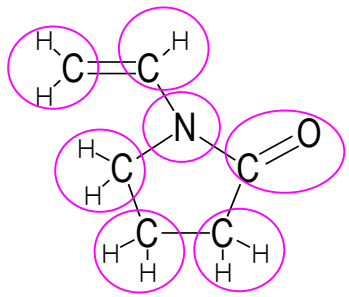
Component	T_c [K]	P_c [bar]	ω
CO_2	304.1[4]	73.8[4]	0.239[4]
NVP	640.6*	42.7*	0.420**

* Estimated with Joback method [5]

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

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

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



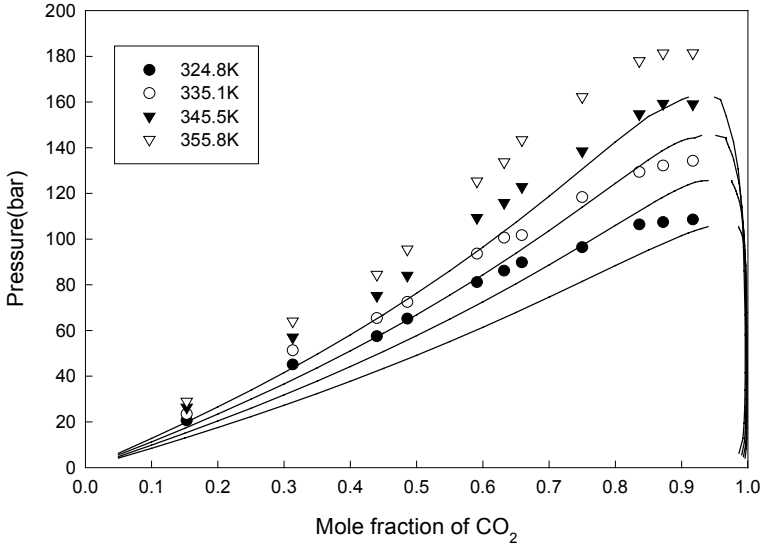
** Estimated with Lee-Kesler method [5]

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

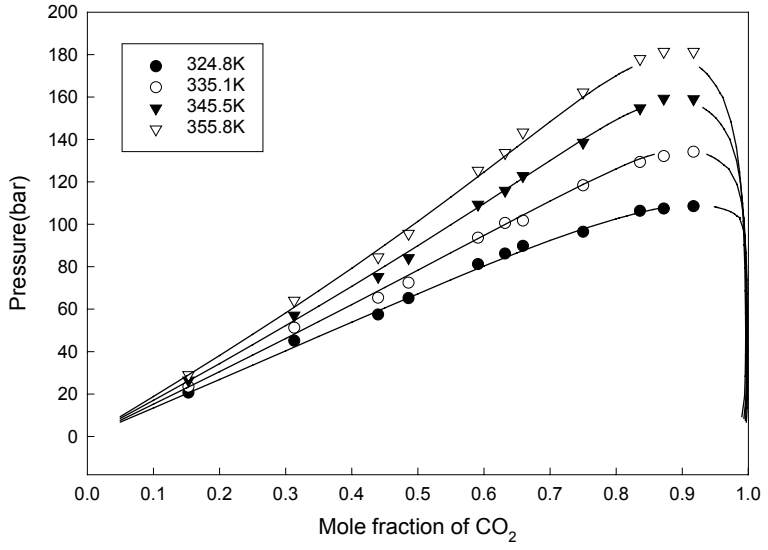
$$\alpha = -\ln P_c - 5.97214 + 6.09648\theta^{-1} + 1.28862 \ln\theta - 0.169347\theta^6$$

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

Correlation of CO_2-NVP System



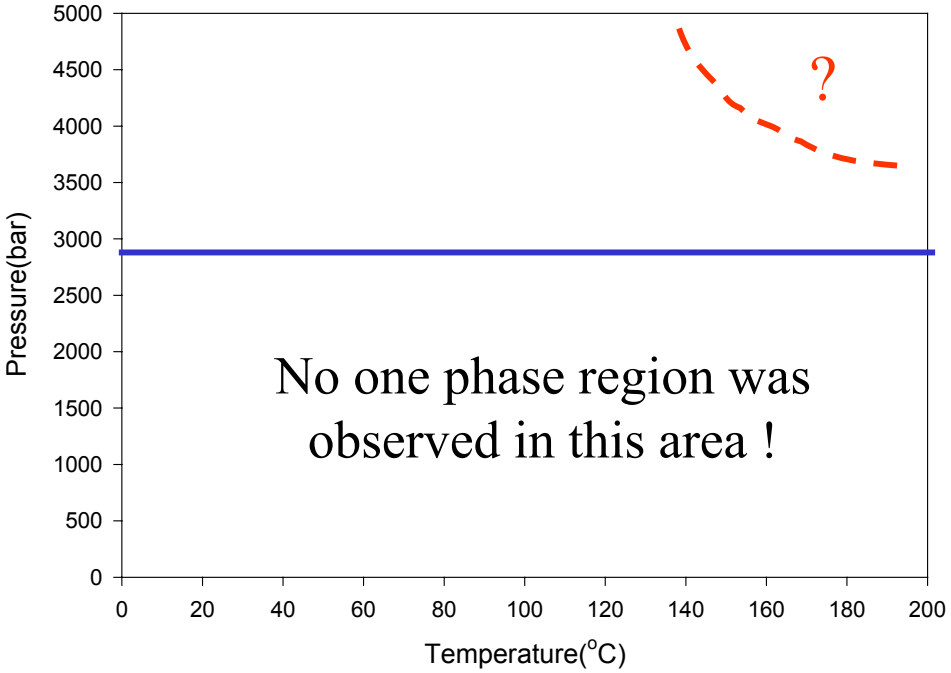
$$k_{ij} = 0.0, \quad \eta_{ij} = 0.0$$



$$k_{ij} = 0.0549, \quad \eta_{ij} = -0.0136$$

$$RMSD\ (\%) = 2.59$$

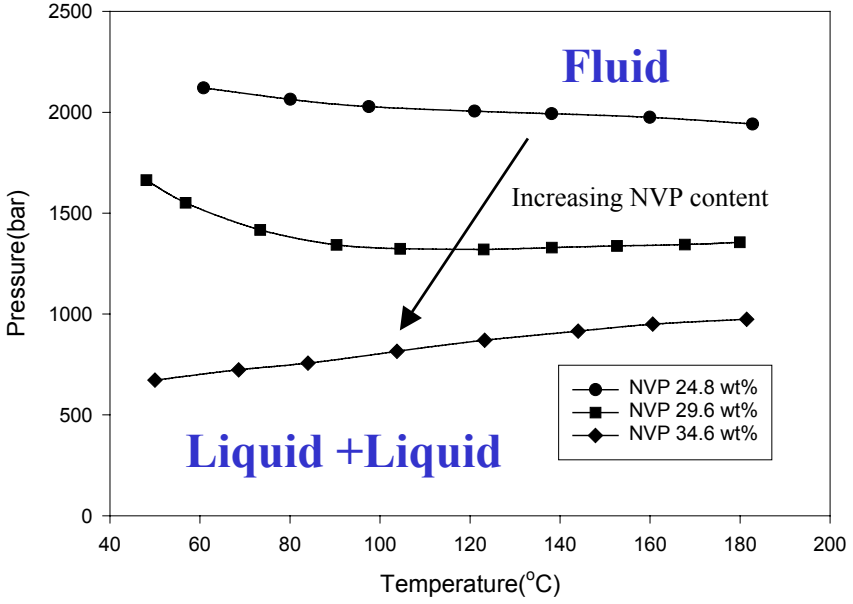
CO_2-PVP System



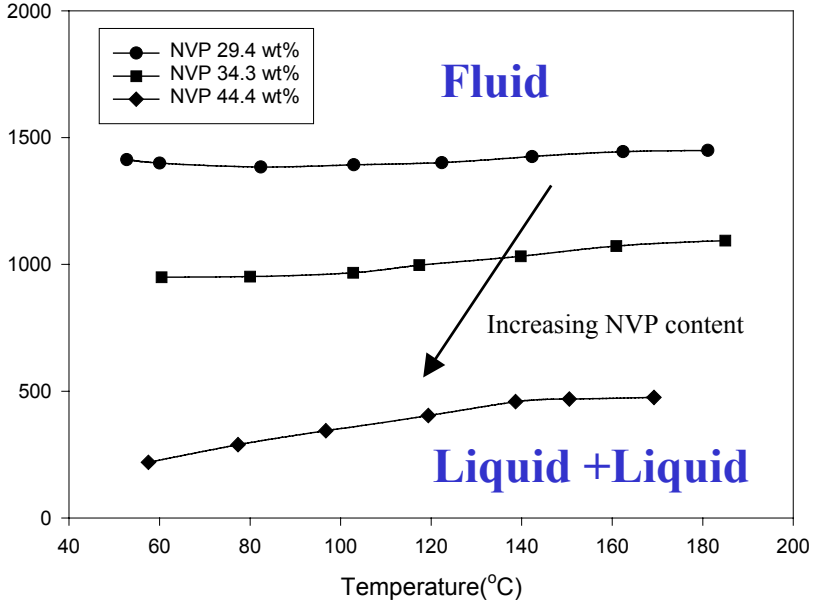
The solubility of PVP in $scCO_2$ was very low !

PVP-NVP-CO_2 system

PVP Mw = 2,500

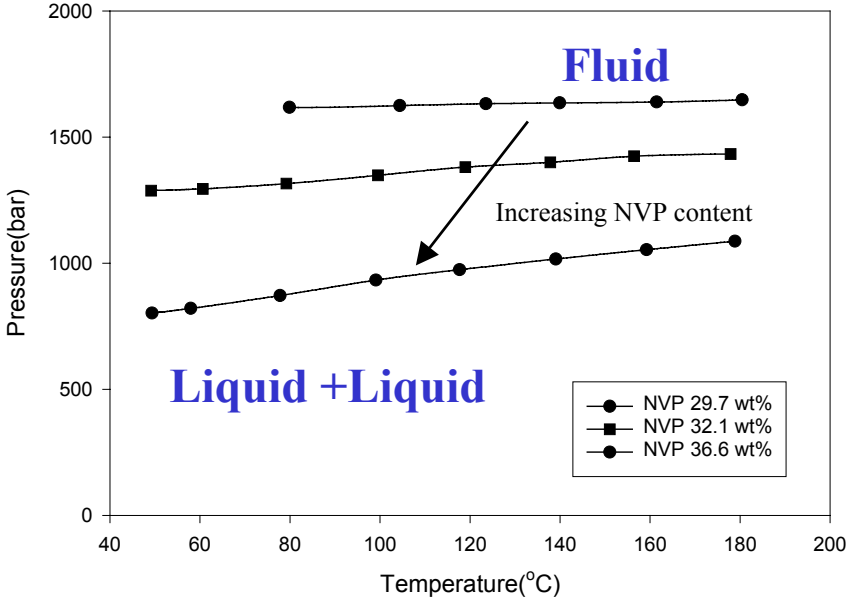


PVP Mw = 10,000

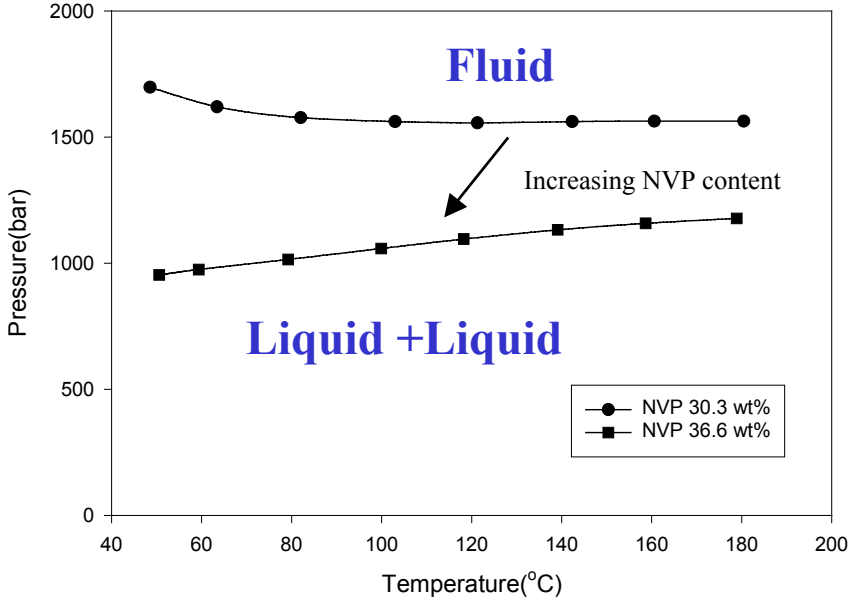


PVP-NVP-CO_2 system

PVP Mw = 29,000



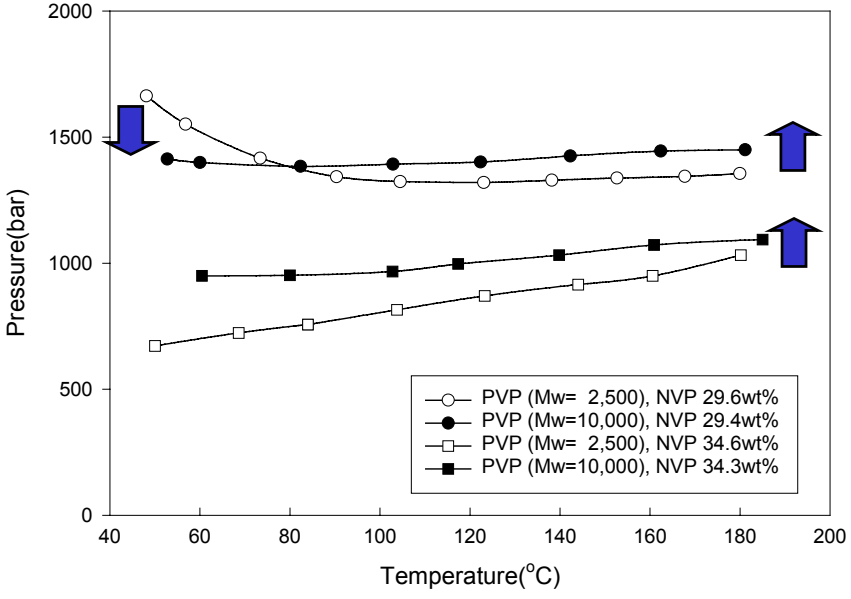
PVP Mw = 55,000



PVP-NVP-CO_2 system with different molecular weight

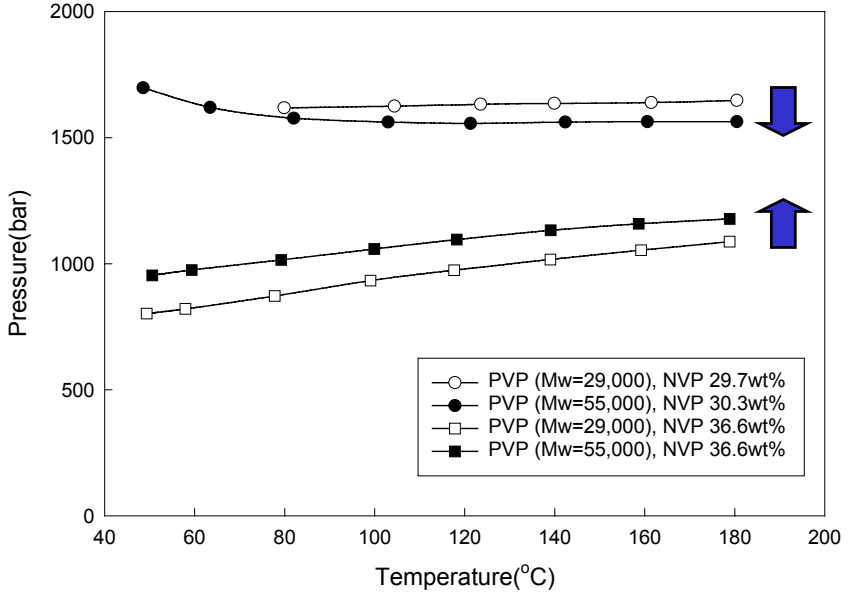
PVP Mw = 2,500

PVP Mw = 29,000



PVP Mw = 29,000

PVP Mw = 55,000



Conclusion

- We measured **pressure – composition(P-x) isotherms** for binary mixture of **CO_2 + NVP system** at temperature from 324K to 355K and pressure up to 190bar.

- We measured **cloud point pressures** for the system **PVP + NVP + CO_2 system** as a function of molecular weight and NVP contents at temperature up to 450K and pressure up to 2,200bar.

- As the NVP content increased, cloud point pressure dramatically decreased.

- But for molecular weight dependency for cloud point pressure, the result is not yet distinct at low NVP content.

Reference

[1] Jennings, D. W., Lee, R. J., Teja, A. S., 1991, Vapor-liquid equilibria in the carbon dioxide + ethanol and carbon dioxide + 1-butanol systems, *J. Chem. Eng. Data*, 36 : 303.

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

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

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

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