Isothermal Vapor-Liquid Equilibria for n-pentane+2-butanol System near the Critical Region

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Introduction

- *VLE and critical point data are of great significance in the various industrial fields to design, simulate and optimize processes.*

- *Alkane + alkanol phase equilibrium data have been extensively investigated at low pressures, but only a few data are available for elevated temperature and pressure.*

- *Furthermore, near the critical region, VLE measurements for polar and non-polar mixtures are especially important because the properties of such mixtures cannot be predicted from the pure component values.*

- *In this work, we have measured the vapor-liquid equilibrium data for the n-pentane + 2-butanol system.*

Apparatus and Materials

Materials

n-Pentane : Fluka with 99.5% purity
2-Butanol : Aldrich with 99.5% purity

Thermometer

Probe : 5614, Indicator : 1560 supplied by Hart Scientific Co.
(accuracy ±0.03K in 373~673K)

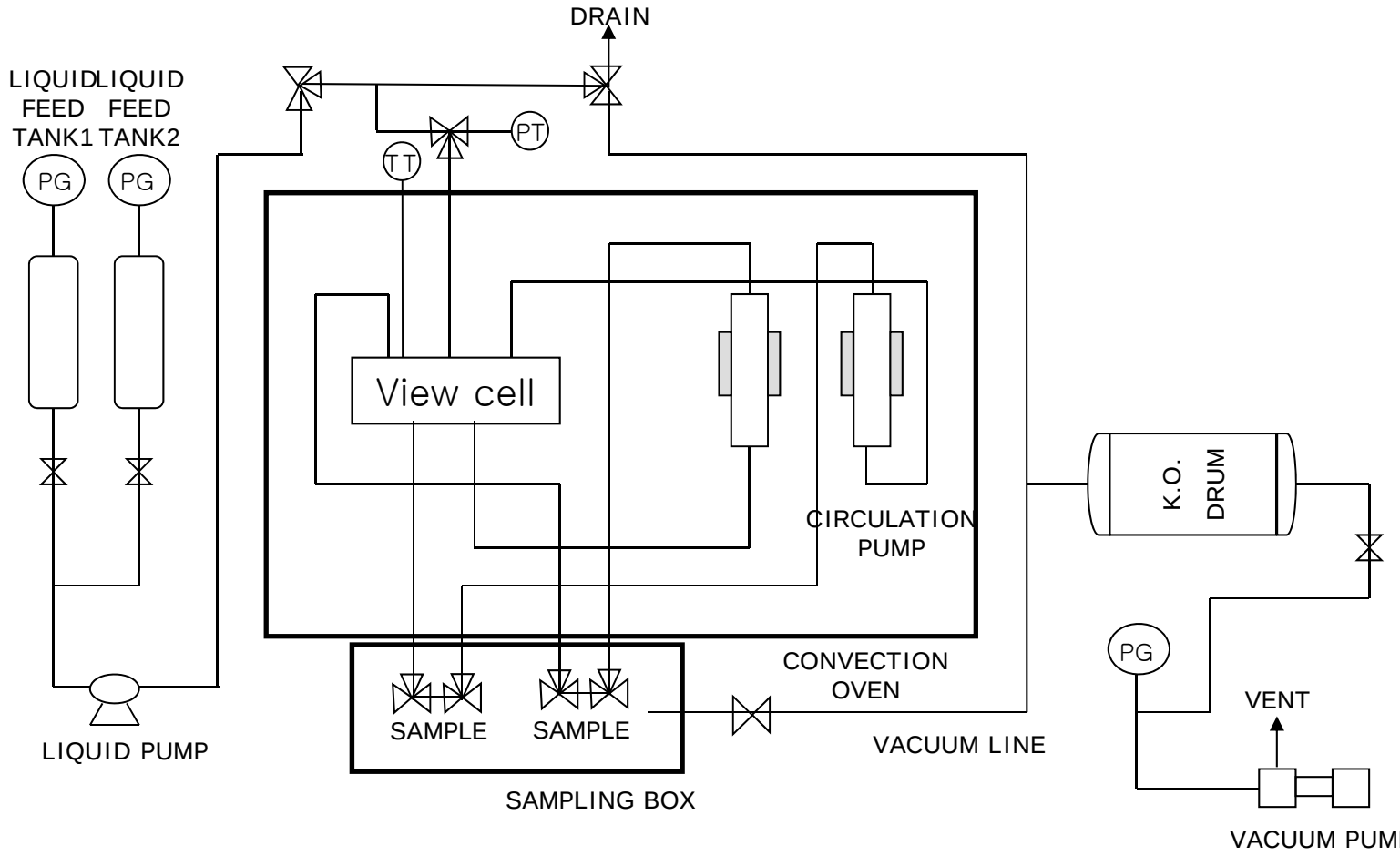
Pressure tranducer

STJE/1833-2 supplied by Sensotec Co.
(range <1000 psia, accuracy ±0.1%)

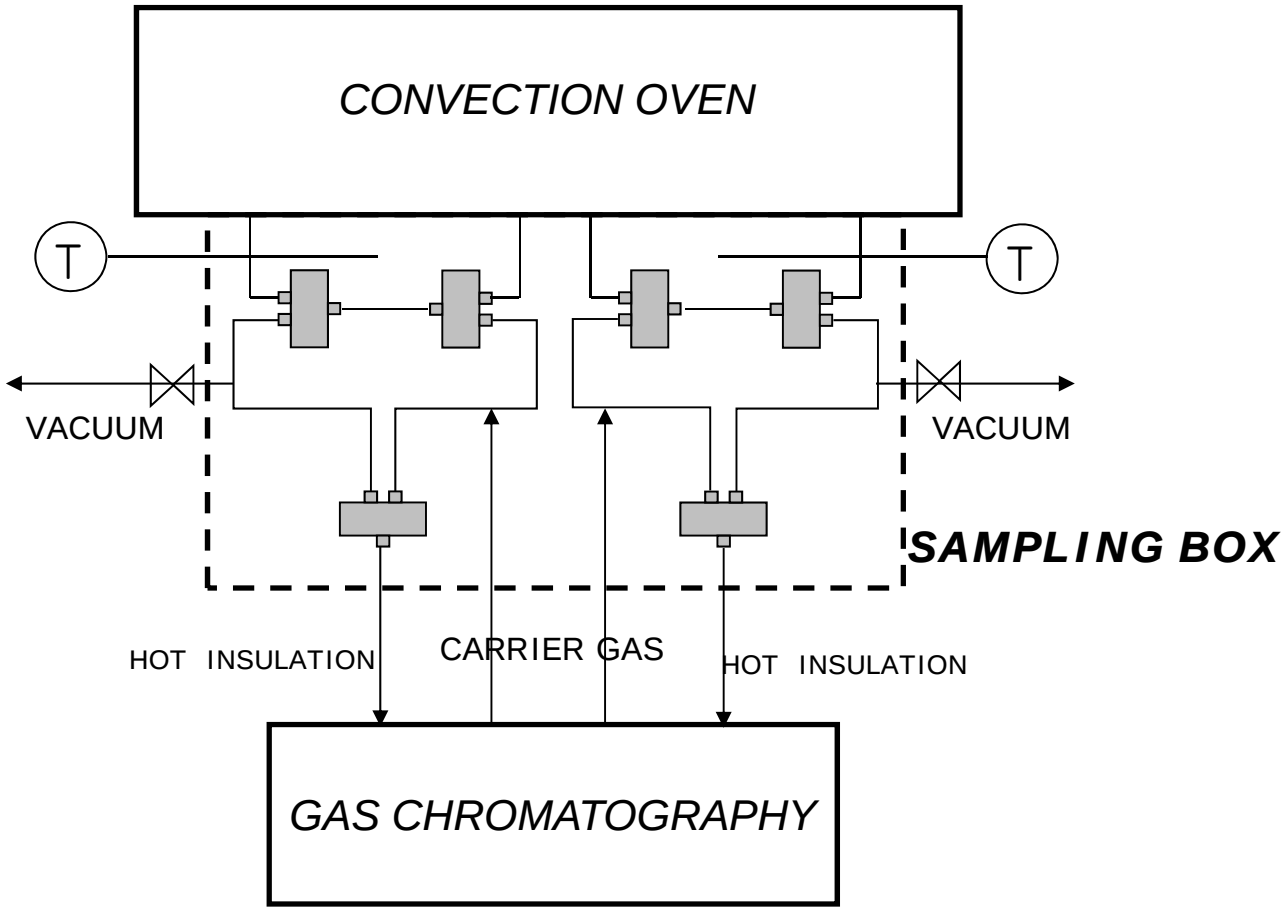
Gas Chromatography

Detector : TCD
Column : Porapak Q in 0.95 cm O.D. and 85 cm long

Apparatus and Materials



Apparatus and Materials



Thermodynamic Models

PRSV

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

$$a(T) = a(T_c)\alpha(T) \qquad b = 0.07780\frac{RT_c}{P_c}$$

$$a(T_c) = 0.45724\frac{(RT_c)^2}{P_c} \qquad \alpha(T) = [1+\kappa(1-\sqrt{T/T_c})]^2$$

Wong-Sandler Mixing Rule

$$b_m = \frac{\sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij}}{1 - \sum_i x_i \frac{a_i}{b_i RT} - \frac{A^E_\infty}{CRT}} \qquad a_m = b_m\left(\sum_i x_i \frac{a_i}{b_i} + \frac{A^E_\infty}{C}\right)$$

NRTL Activity coefficient Model

$$\frac{A^E_\infty}{RT} = \sum_{i=1}^{n} x_i \frac{\sum_{j=1}^{n} x_j G_{ji} \tau_{ji}}{\sum_{k=1}^{n} x_k G_{kj}} \qquad G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \qquad \tau_{ji} = \frac{g_{ji}}{RT}$$

Thermodynamic Models

Multi-Fluid Nonrandom Lattice Fluid with Hydrogen Bonding Equation of State (MF-NLF-HB)

$$P = \frac{1}{\beta V_H}\left\{\frac{z}{2}\ln\left[1+\left(\frac{q_M}{r_M}-1\right)\rho\right]-\ln(1-\rho)-(\upsilon_H-\upsilon_{H0})\rho+\frac{z}{2}\sum_{i=1}^{c}\theta_i\left(\frac{\tau_{0i}}{\sum_{k=0}^{c}\theta_k\tau_{ki}}-1\right)\right\}$$

where $\tau_{ji} = \exp\left[\beta(\varepsilon_{ji}-\varepsilon_{ii})\right]$

The coordination number : z =10

Lattice volume : V_H = 9.75 cm^3/mol

Pure parameters (r_i, ε_{ii}) :

$$r_i = r_a + r_b(T - T_0) + r_c[T\ln(T_0/T) + T - T_0]$$
$$\varepsilon_{ii}/k = e_a + e_b(T - T_0) + e_c[T\ln(T_0/T) + T - T_0]$$

- *Binary parameter (λ_{ij}) :* $\varepsilon_{12} = (\varepsilon_{11}\,\varepsilon_{22})^{1/2}(1-\lambda_{12})$

Correlation

PRSV-WS-NRTL

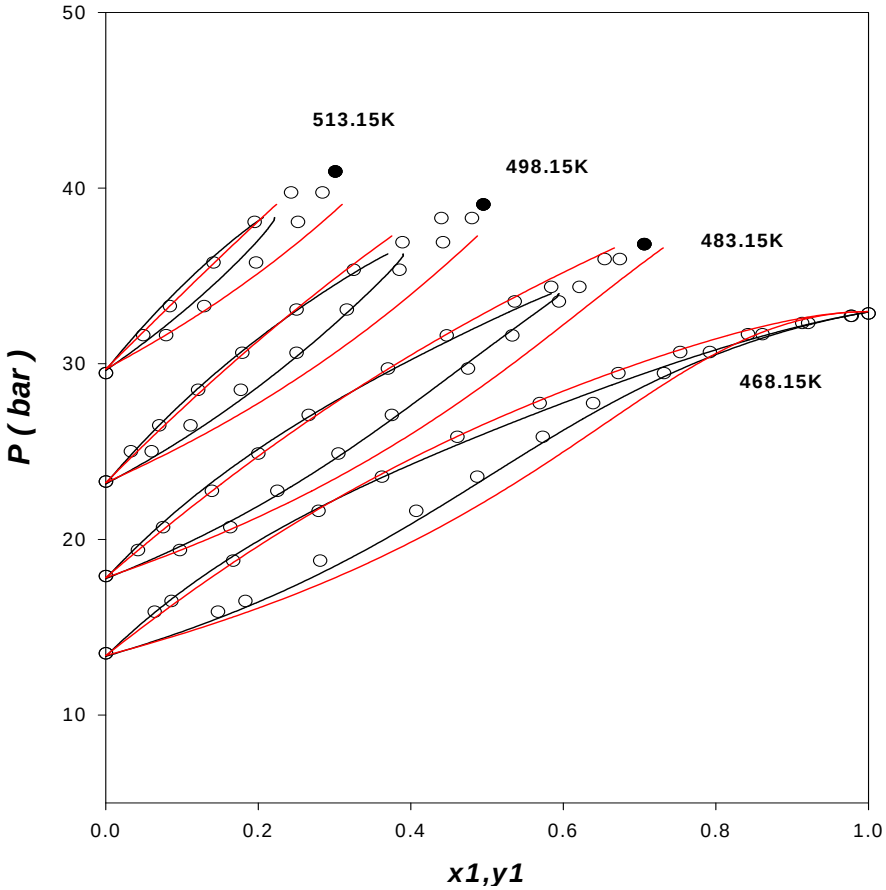
NRTL Parameters (468.15K)

α	g_{12} (cal/mol)	g_{21} (cal/mol)
0.3	483.15	650.40

MF-NLF-HB

	E_a	E_b	E_c	R_a	R_b	R_c
n-Pentane	64.5926	0.4962	1.3096	14.9330	-0.8508	-2.3118
2-Butanol	76.4709	0.2867	0.5009	7.6963	-0.0896	-0.3451

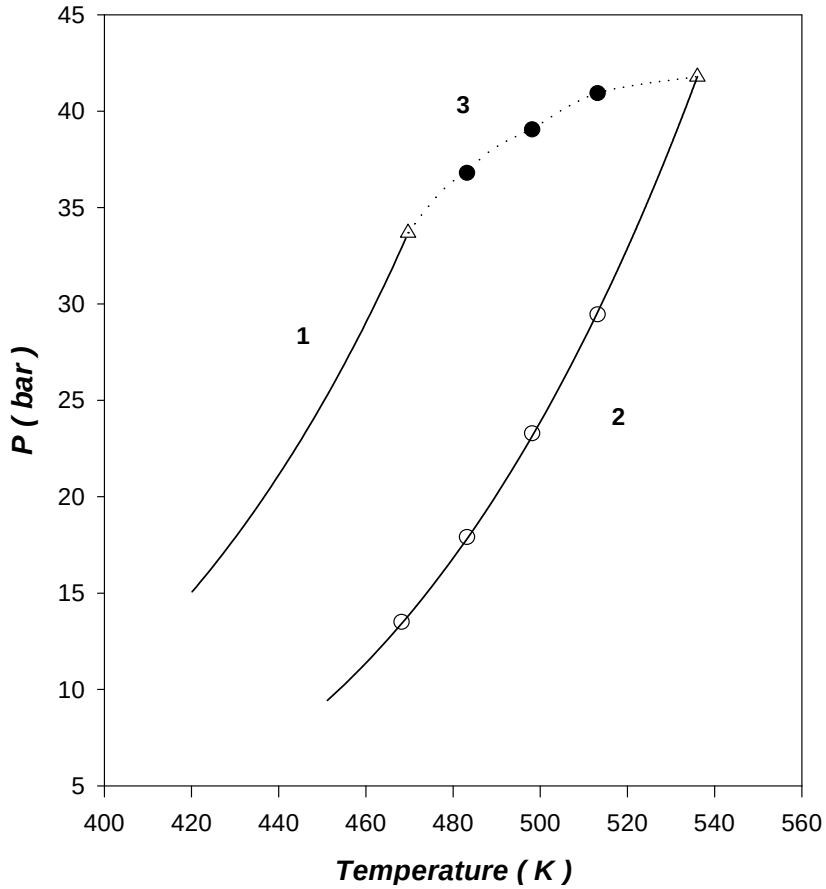
Correlation



Comparison of measured data with correlation values for n-pentane (1) + 2-butanol (2)

●, *critical points;*
——, *calculated by PRSV-WS EOS;*
——, *calculated by MF-NLF-HB EOS.*

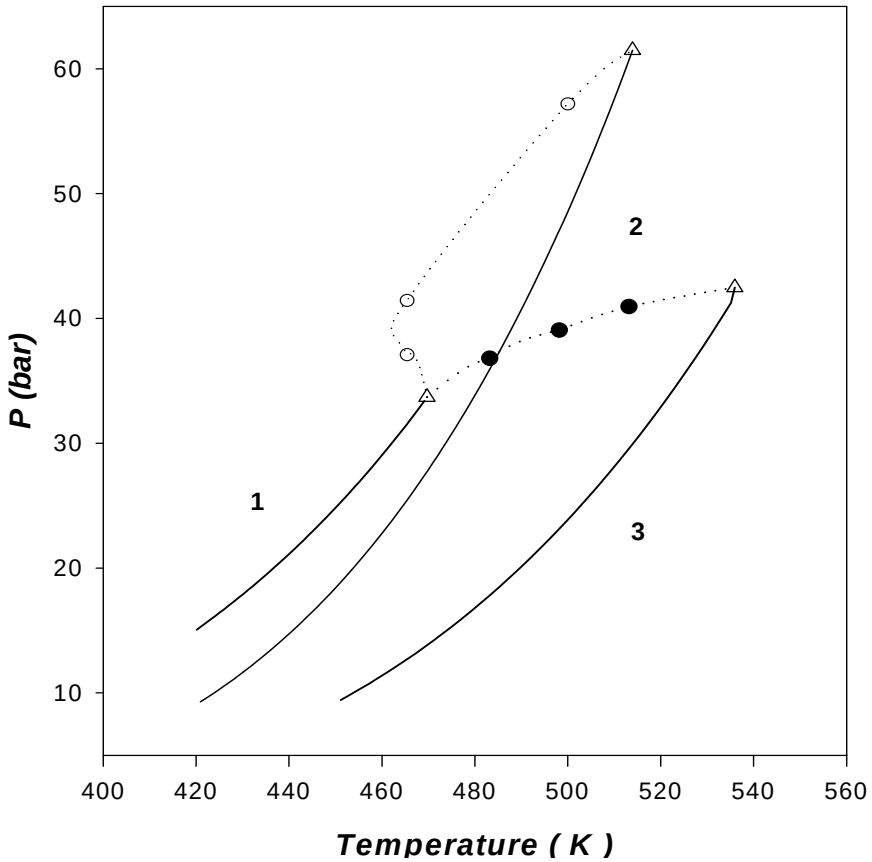
Critical locus



Critical locus and pure vapor pressure curve for n-pentane (1) ,2-butanol(2) and critical locus (3):

●, *critical points;*
○, *pure vapor pressure points from this work;*
△, *critical points of pure components from the data bank by Reid et al.;*
····· *(3) , interpolation curve of critical points.*

Critical locus



Critical locus and pure vapor pressure curves for n-pentane (1), ethanol (2), 2-butanol (3):

●, this work;
○ ,Seo et al.[Fluid Phase Equilib. (2000) 172];
Δ, critical points of pure components ;
····· , interpolation curve

Correlation Errors

T (K)	Model	λ_{ij}	$100\sqrt{SQP / N_T}$	$\sqrt{SQY / N_T}$
468.15	PRSV-WS	0.02017	1.14	0.019
	MF-NLF-HB	-0.01799	0.96	0.044
483.15	PRSV-WS	0.01562	1.23	0.018
	MF-NLF-HB	-0.02262	0.75	0.045
498.15	PRSV-WS	0.02346	0.46	0.022
	MF-NLF-HB	-0.02361	1.19	0.044
513.15	PRSV-WS	0.00811	1.15	0.020
	MF-NLF-HB	-0.03709	0.33	0.026

$$SQP = \left((P_{cal} - P_{\exp}) / P_{\exp}\right)^2 \quad SQY = (y_{1.cal} - y_{1.\exp})^2$$

Conclusion

- *The isothermal VLE data for the system n-pentane + 2-butanol were obtained at 468.15, 483.15, 498.15 and 513.15 K.*
- *Critical points were found at 483.15, 498.15 and 513.15K.*
- *The MF-NLF-HB EOS and PRSV EOS combined with NRTL model and Wong-Sandler mixing rules for correlating parameters resulted in a good agreement with experimental data in the sub-critical regions. However, the MF-NLF-HB EOS has shown larger deviation in experimental data near the critical region than PRSV EOS.*
- *The fitted parameter from VLE data near critical region gave a guidance to calculate and predict critical loci.*