Isothermal Vapor-Liquid Equilibria for *n*-Hexane + 1-Propanol System near Critical Region

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Introduction

- *VLE and critical point data are of great significance in the various industrial fields to design, simulation and optimization of processes.*
- *Alkane + alkanol phase equilibrium data has been extensively investigated at low pressures, but only a few data 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 1-propanol + n-hexane system.*

Apparatus and Materials

Materials

n-Hexane : Fluka with a 99.5% purity
1-Propanol : ALDRICH with a 99.5% purity

Thermometer

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

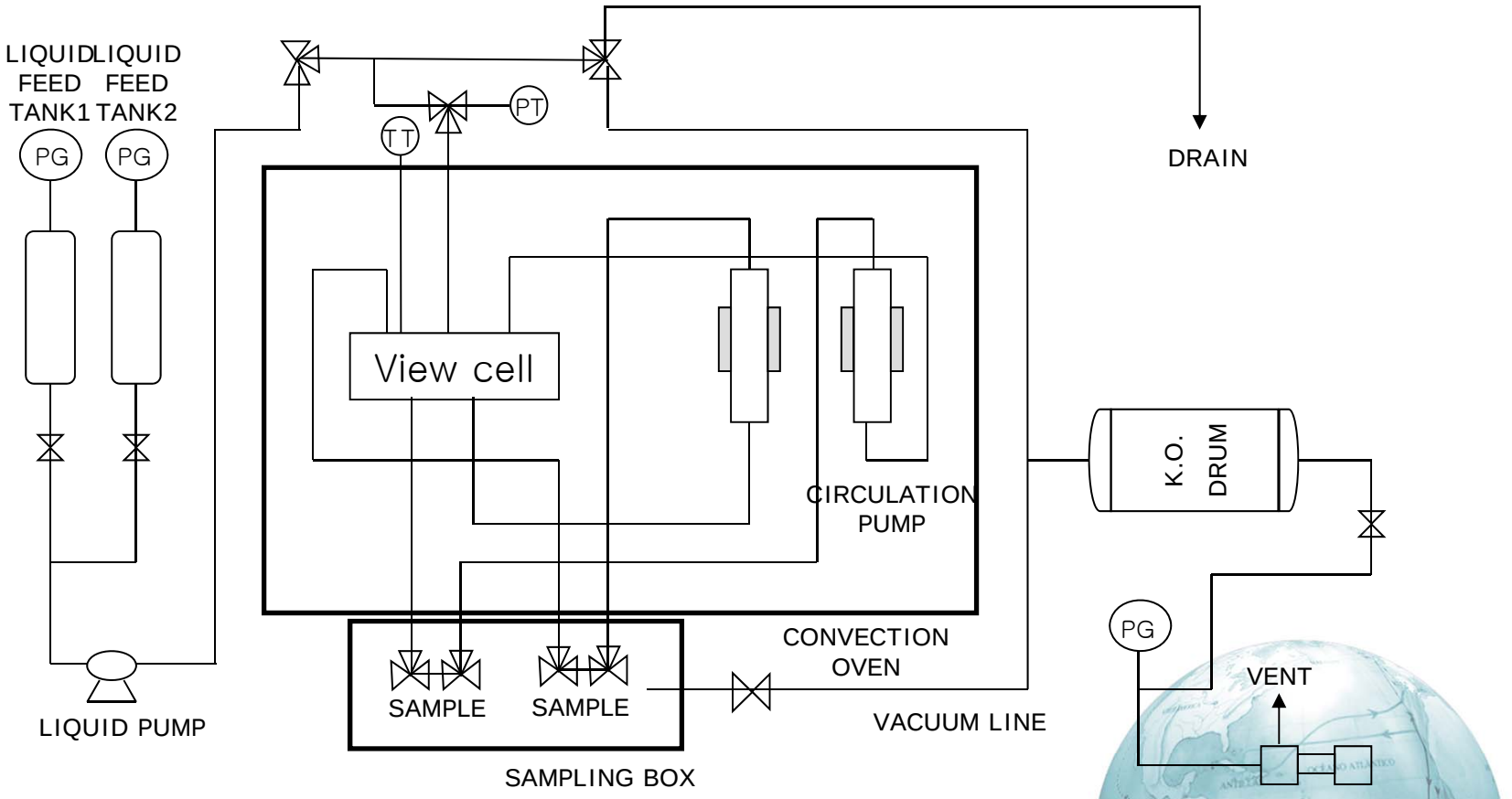
Pressure tranducer

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

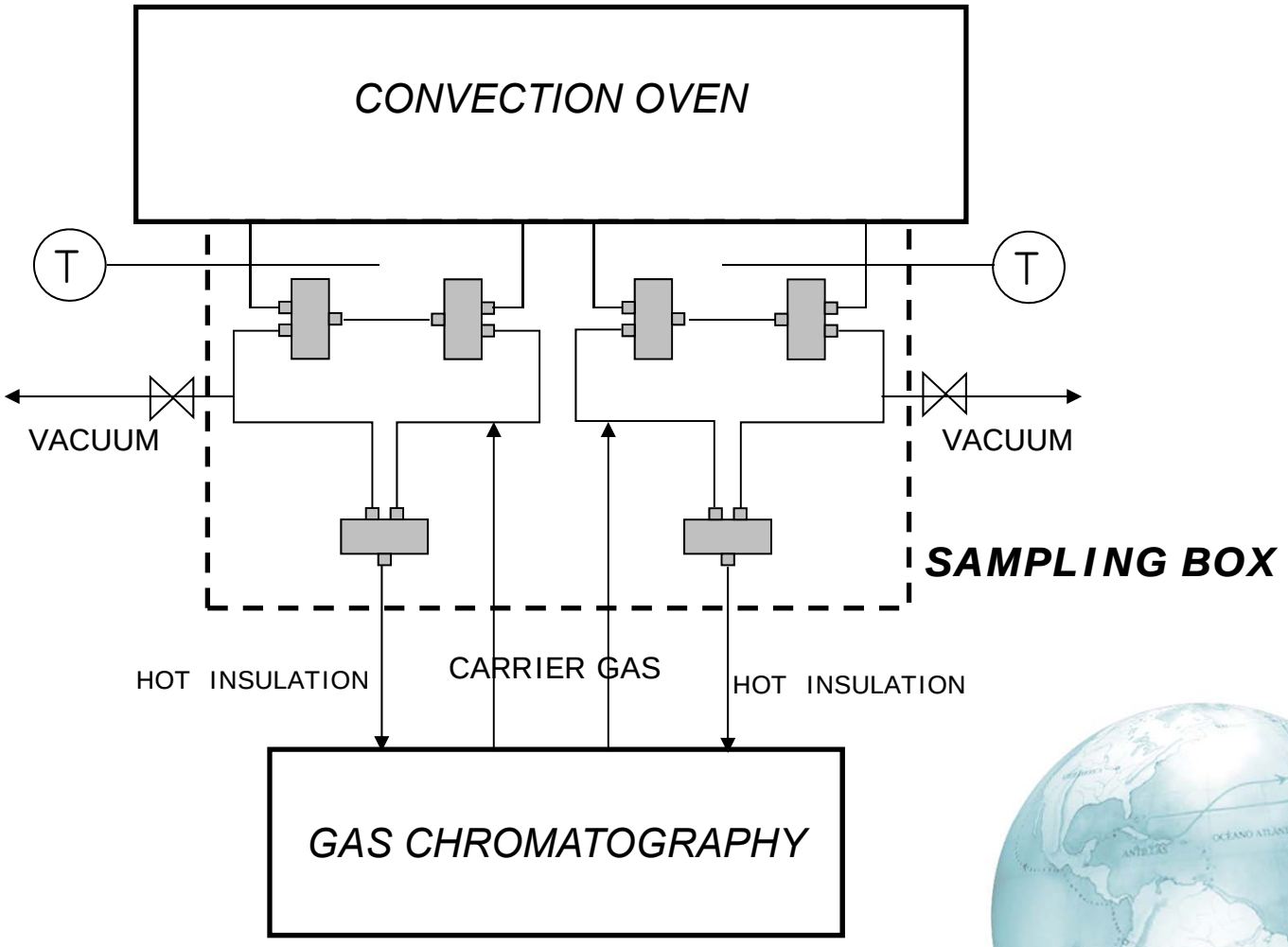
Gas Chromatography

Model : DS6200 ; Detector : TCD
Column : Porapak Q in 0.95 cm O.D. and 85 cm long

Experimental Apparatus



Experimental Apparatus – Sampling Box



Measured VLE Data of the n-Hexane + 1-Propanol System

P (bar)	x_1	y_1	P (bar)	x_1	y_1
T = 483.15K			T = 493.15K		
20.88	0.000	0.000	25.07	0.000	0.000
21.38	0.015	0.038	26.00	0.029	0.054
22.05	0.035	0.065	28.00	0.096	0.155
24.85	0.146	0.248	30.82	0.247	0.319
26.75	0.322	0.371	31.81	0.354	0.406
27.35	0.401	0.432	32.12	0.421	0.441
27.58	0.450	0.471	32.15	0.473	0.494
27.71	0.519	0.515	31.60	0.619	0.592
27.15	0.642	0.613	31.06	0.684	0.647
25.96	0.730	0.681	29.87	0.759	0.727
23.29	0.904	0.859	29.25	0.807	0.756
21.71	0.981	0.961	28.22	0.852	0.808
21.27	1.000	1.000	26.20	0.942	0.913
			24.51	1.000	1.000

Measured VLE Data of the n-Hexane + 1-Propanol System

P (bar)	x_1	y_1	P (bar)	x_1	y_1
T =503.15K			T = 513.15K		
30.09	0.000	0.000	35.54	0.000	0.000
31.97	0.061	0.103	37.14	0.034	0.064
34.47	0.179	0.224	40.40	0.134	0.181
36.34	0.291	0.325	42.12	0.238	0.265
37.18	0.362	0.385	43.13	0.300	0.307
37.54	0.404	0.421	43.32	0.312	0.317
37.75	0.432	0.449	43.40	0.139	CP
37.88	0.495	0.502			
37.58	0.541	0.533			
37.05	0.599	CP			
34.07	0.786	CP			
33.33	0.829	0.814			
32.74	0.853	0.835			
31.90	0.888	0.864			
29.64	0.954	0.935			
28.24	1.000	1.000			

CP : Critical Point

Thermodynamic Models

Modified Peng-Robinson Equation of state with Wong-Sandler mixing rule

$$P = \frac{RT}{v-b} - \frac{a}{v^2 + 2bv - b^2}$$

$$a = (0.457235\ R^2 T_c^2 / P_c)\alpha$$

$$b = 0.77796\ RT_c / P_c$$

$$\alpha = [1 + \kappa(1 - T_R^{0.5})]^2$$

$$\kappa = \kappa_0 + \kappa_1(1 + T_R^{0.5})(0.7 - T_R)$$

$$\kappa_0 = 0.378893 + 1.4897153\,\omega - 0.17131848\,\omega^2 + 0.0196554\,\omega^3$$

$$b_m = \frac{\sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij}}{1 - \sum_i x_i \frac{a_i}{b_i RT} - \frac{A_\infty^E}{CRT}}$$

$$a_m = b_m \left(\sum_i x_i \frac{a_i}{b_i} + \frac{A_\infty^E}{C} \right)$$

NRTL Activity coefficient Model

$$\frac{A_\infty^E}{RT} = \sum_{i=1}^{n} x_i \frac{\sum_{j=1}^{n} x_j G_{ji} \tau_{ji}}{\sum_{k=1}^{n} x_k G_{kj}} \quad \textit{with} \quad G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \quad \textit{where} \quad \tau_{ji} = \frac{g_{ji}}{RT}$$

Thermodynamic Models

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

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

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 Parameters

PRSV-WS-NRTL

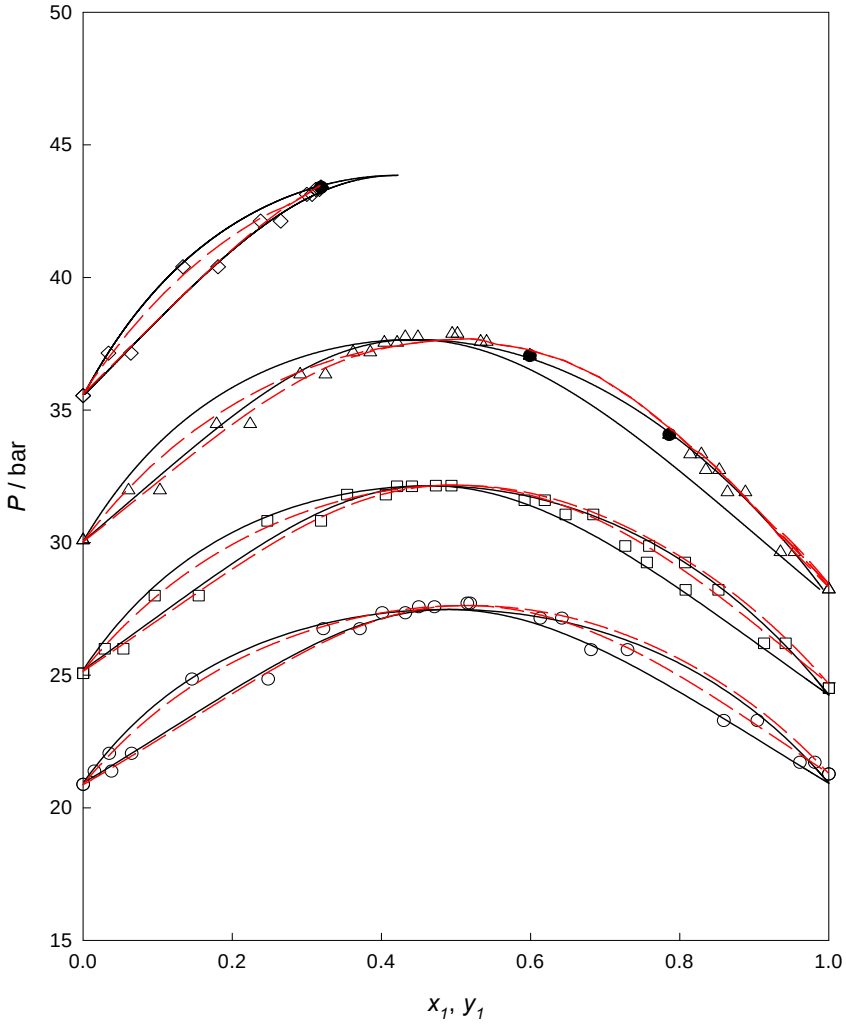
g_{12}	g_{21}	α
1092.147	480.674	0.294

45℃ data : Brown I., Fock W., Smith F., *J. Chem. Thermodyn.*, 1, *273*(1969)

MF-NLF-HB

	E_a	E_b	E_c	R_a	R_b	R_c
n-Hexane	96.84253	0.01474	-0.03550	11.07715	-0.00017	0.00391
1-Propanol	89.39176	0.11388	0.08600	6.25494	0.00286	-0.00204

Correlation Results

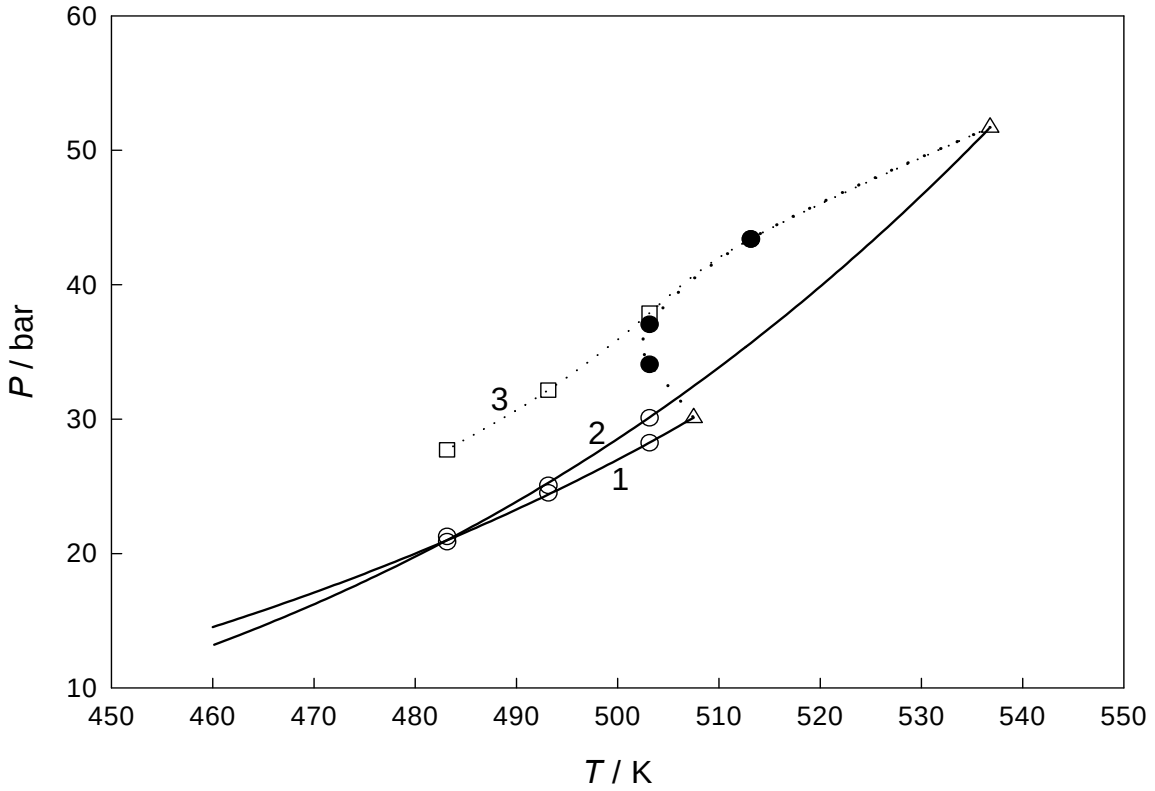


Comparison of measured data with correlation values for n-hexane (1) + 1-propanol (2)

○, 483.15K; □, 493.15K;
Δ, 503.15K; ◇, 513.15K;
●, critical points;

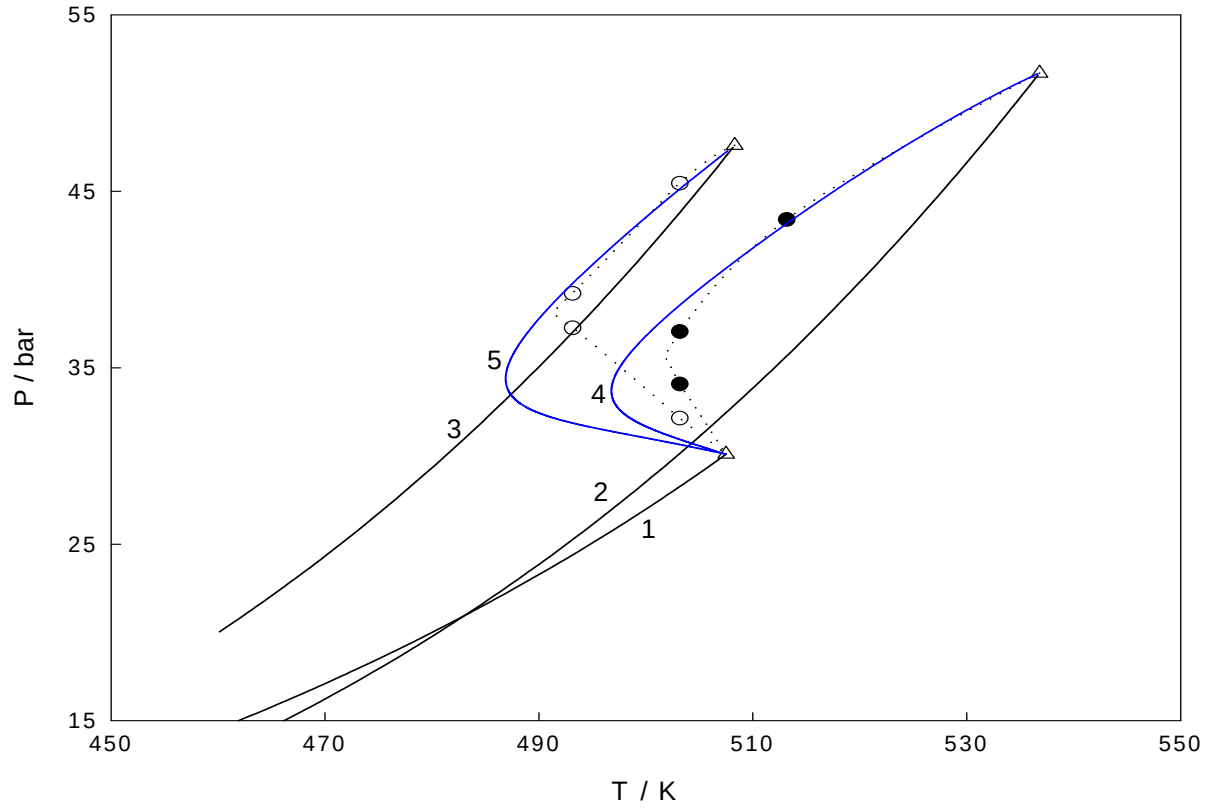
– – –, calculated by PRSV-WS EOS;
——, calculated by MF-NLF-HB EOS.

Critical Locus



Critical locus and pure vapor pressure curve for n-hexane (1), 1-propanol (2), and an azeotropic mixture (3):
●, critical points; ○, pure vapor pressure points from this work;
□, azeotrope points; △, critical points of pure components
…… , interpolation curve of experimental data; —— , vapor pressure curve.

Critical Locus



Critical locus and pure vapor pressure curves for n-hexane (1), 1-propanol (2), 2-propanol (3):
●, this work; ○ ,Seo et al.[J. Chem. Eng. Data 48 (2003) 856];
Δ, critical points of pure components ; ·····, interpolation curve;
—— (4), critical locus calculation for n-hexane + 1-propanol system;
—— (5), critical locus calculation for n-hexane + 2-propanol system;
using PRSV-WS EOS.

Correlation Errors

T (K)	Model	k_{12}	AADP[a]	AADY[b]
483.15	PRSV-WS	0.1312	0.679	0.039
	MF-NLF-HB	0.0267	0.652	0.009
493.15	PRSV-WS	0.1188	0.499	0.040
	MF-NLF-HB	0.0285	0.420	0.013
503.15	PRSV-WS	0.1233	0.433	0.028
	MF-NLF-HB	0.0332	0.697	0.016
513.15	PRSV-WS	0.1516	0.313	0.070
	MF-NLF-HB	0.0375	0.345	0.011

$$^{a}AADP = (100/n_{\mathrm{T}})\sum_i^N \left| P_i^{calc} - P_i^{\exp} \right| / P_i^{\exp}$$

$$^{b}AADY = (1/n_{\mathrm{T}})\sum_i^N \left| y_i^{calc} - y_i^{\exp} \right| / y_i^{\exp}$$

Conclusion

- *The isothermal VLE data for the system n-hexane + 1-propanol were obtained at 483.15, 493.15, 503.15 and 513.15 K.*
- *Critical points were found at 503.15 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 an experimental data in the sub-critical regions. However, the prediction of critical pressure has shown a large deviation in experimental data.*
- *The fitted parameter from VLE data near critical region gave a guidance to calculate and predict critical loci.*