Application of Multi Fluid Nanrandom Lattice Fluid Model to Complex Systems

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Historical Background of MF-NLF-HB EOS

NLF EOS

Fluid Phase Equilibria, 93, 193(1994): 93, 215(1994):
95, 2773(1995): 151, 191-198 (1998)
J. of Supercritical Fluids (1993, 1995)
Int. J. of Thermodynamics (1995) etc.

NLF-HB EOS

Fluid Phase Equilibria, 158, 143-149, (1999)

Fluid Phase Equilibira, 4883, 1-9 (2001)

MF-NLF EOS

Bull. of Korea Chem. Soc.18, 841-850 (1997): 18, 965-872 (1997)
Fluid Phase Equilibria, 150-151, 191 (1998), etc

MF-NLF-HB EOS

J. of Supercritical Fluids, 189, 49-61. (2001)
Korean J. Chem. Eng. 20, 911-915 (2003)

The NLF-HB Equation of State

$$p = \frac{1}{\beta V_H}\left\{\frac{z}{2}\ln\left[1+\left(\frac{q_M}{r_M}-1\right)\rho\right]-\ln(1-\rho)-(\nu_{HB}-\nu_{HB0})\rho\right\}-\frac{z\varepsilon_M}{2V_H}\theta^2$$

where

$$\varepsilon_M = \frac{1}{\theta^2}\left[\sum\sum\theta_i\theta_j\varepsilon_{ij}+\frac{\beta}{2}\sum\sum\sum\sum\theta_i\theta_j\theta_k\theta_l\varepsilon_{ij}\left(\varepsilon_{ij}+3\varepsilon_{kl}-2\varepsilon_{ik}-2\varepsilon_{jk}\right)\right]$$

$$\varepsilon_{ij} = \left(\varepsilon_{ii}\varepsilon_{jj}\right)^{1/2}\left(1-\lambda_{ij}\right)$$

The MF-NLF-HB Equation of State

$$P = \frac{1}{\beta V_{\mathrm{H}}}\left\{\frac{z}{2}\ln\left[1+\left(\frac{q_{\mathrm{M}}}{r_{\mathrm{M}}}-1\right)\rho\right]-\ln(1-\rho)-(\upsilon_{\mathrm{HB}}-\upsilon_{\mathrm{HB0}})\rho+\frac{z}{2}\sum_{i=1}^{c}\theta_i\left(\frac{\tau_{0i}}{\sum_{k=0}^{c}\theta_k\tau_{ki}}-1\right)\right\}$$

◆ **Liquid Liquid Equilibiria of Polymer Solutions**

-LLE of high Pressure

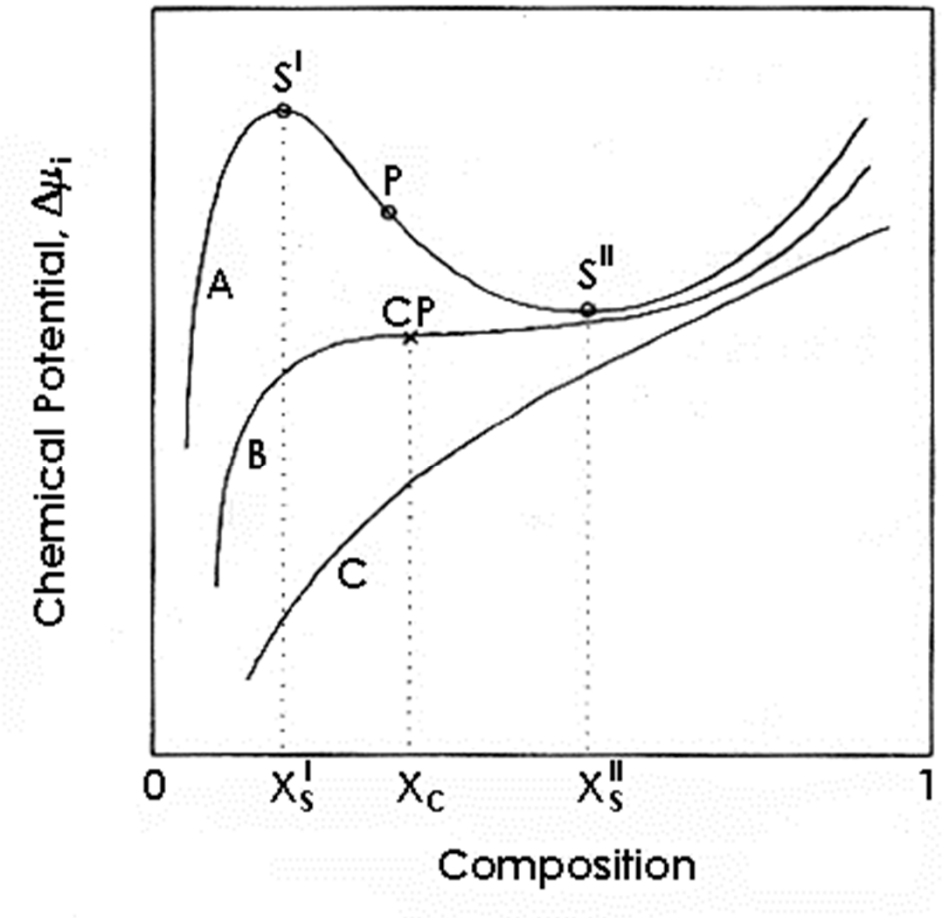
-LLE of high molecular weight component

◆**High Pressure VLE of hydrogen bonding components**

-water + hydrocarbon systems

-critical loci

Liquid-Liquid Equilibria (LLE)



$\Delta\mu_i^I = \Delta\mu_i^{II}$: Binodal composition

$\left(\frac{\partial \Delta\mu_i}{\partial x}\right)_{T,P} = 0$: Spinodal composition

$\left(\frac{\partial \Delta\mu_i}{\partial x}\right)_{T,P} < 0$: Phase split

Three Different Types of chemical potentials as a function of composition in Liquid-Liquid Equilibria

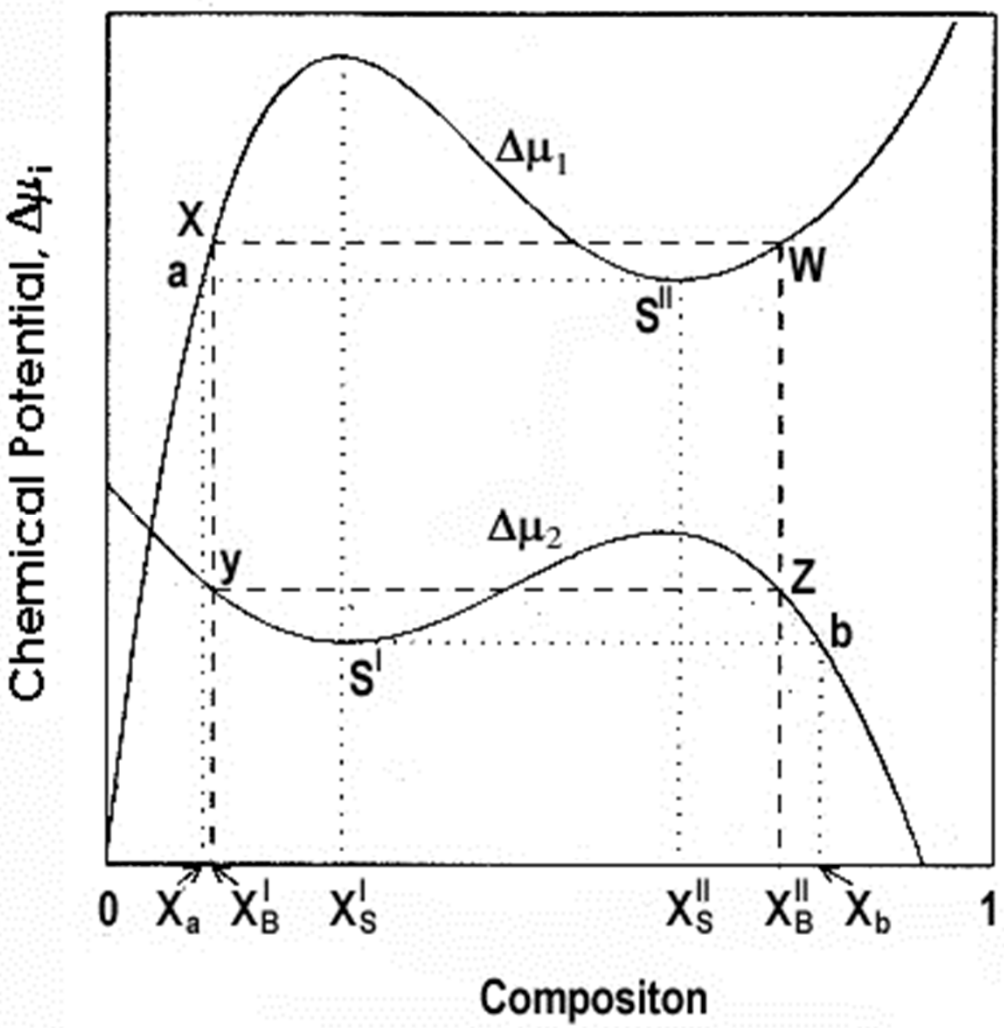


Fig. Chemical Potential of each component as a function of composition in a binary system where phase splitting occurs

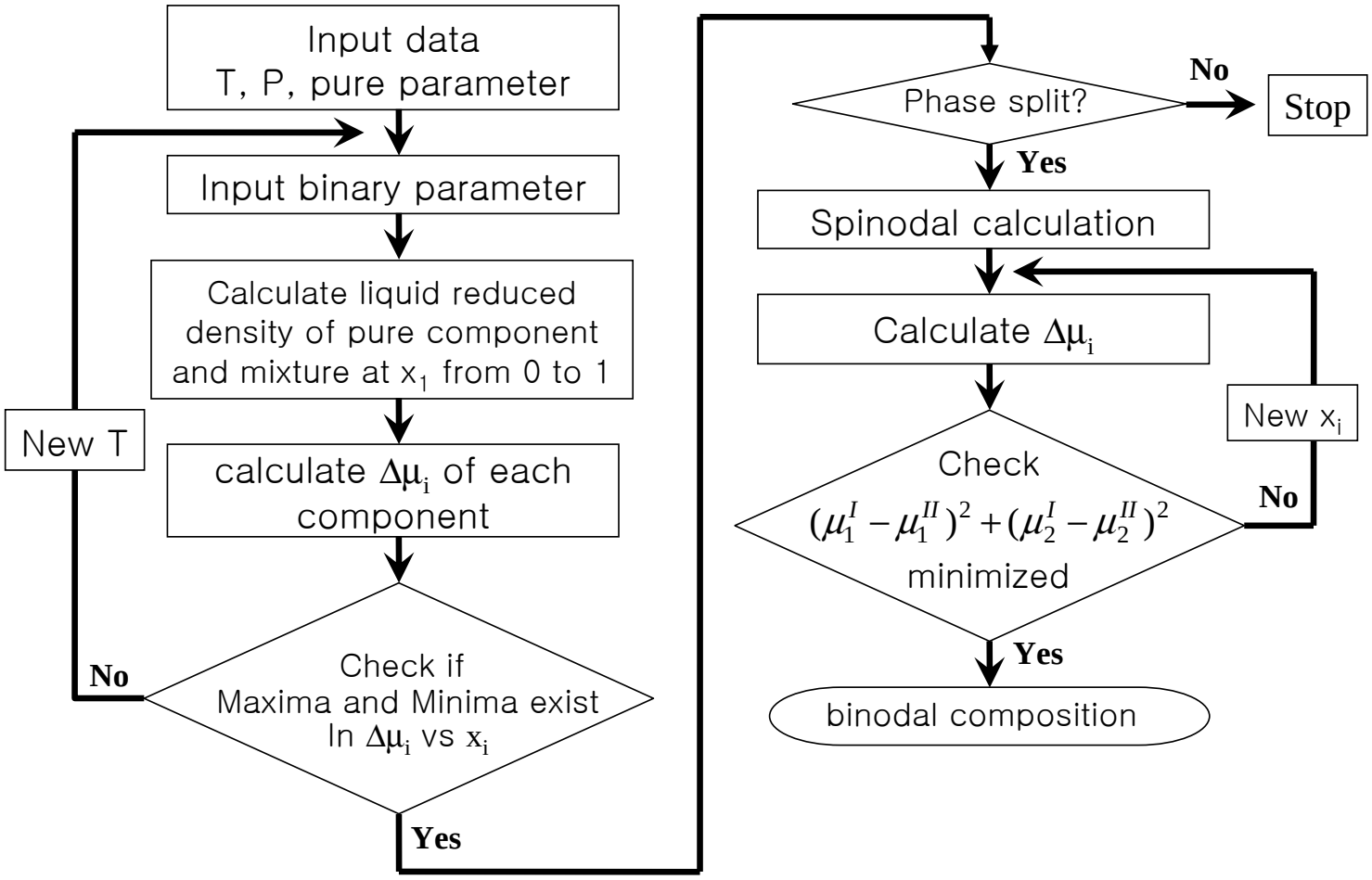

Input data
T, P, pure parameter
Input binary parameter
Calculate liquid reduced density of pure component and mixture at x_1 from 0 to 1
calculate $\Delta\mu_i$ of each component
Check if Maxima and Minima exist In $\Delta\mu_i$ vs x_i
No
Yes
New T
Phase split?
No
Stop
Yes
Spinodal calculation
Calculate $\Delta\mu_i$
Check $(\mu_1^I - \mu_1^{II})^2 + (\mu_2^I - \mu_2^{II})^2$ minimized
No
New x_i
Yes
binodal composition

Table . Energy and size parameters of MF-NLF EOS

	E_a	E_b	E_c	R_a	R_b	R_c
	K	-	-	cm^3/mol^* or, cm^3/g^{**}	$cm^3/mol\,K$	$cm^3/mol\,K$
Pentane	93.98580	0.00956	-0.04549	9.60920*	.00007	.00396
Hexane	96.84253	0.01474	-0.03550	11.07715*	-.00017	.00391
Polyisobutylene	129.80899	.09884	-	0.10311**	-	-
Polyethylene	126.19111	.07192	-	0.11320**	-	-
Polybutadiene	119.88012	.16455	-	0.10344**	-	-
Polystyrene	130.90941	.08278	-	0.06010**	-	-

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

$$r_i = r_a + r_b(T - T_0) + r_c[T\ln(T_0/T) + T - T_0]$$

Binary parameters and error % for liquid-liquid equilibria of polymer solution

System	Range		Fitting parameter for binary parameter ($\lambda_{12} = a + bT + cT^2$)			Error %	
	T(K)	P(MPa)	*a*	b	c	ΔP	ΔT
PE/hexane	421.15~ 433.15	6.0	-4.64488	1939.28	-204.196	-	0.34
PIB/pentane	374.15~ 476.15	1.2~ 23.6	-0.96750	514.660	-71.8000	2.47	-
PIB/hexane	413.15~ 493.15	1.1~ 15.1	-0.85310	415.320	- 54.2440	5.15	-
PE/pentane	393.15~ 493.15	6.9~ 22.3	-0.28190	184.780	-31.6960	2.48	-
PBD/PS	350.83~ 399.47	0.1~101.3	0.00944	-1.20430	0	-	1.42

$$\Delta P = \frac{1}{N}\left(\left|P^{\exp} - P^{\mathrm{cal}}\right| / P^{\exp}\right)\times 100 \qquad \Delta T = \frac{1}{N}\left(\left|T^{\exp} - T^{\mathrm{cal}}\right| / T^{\exp}\right)\times 100$$

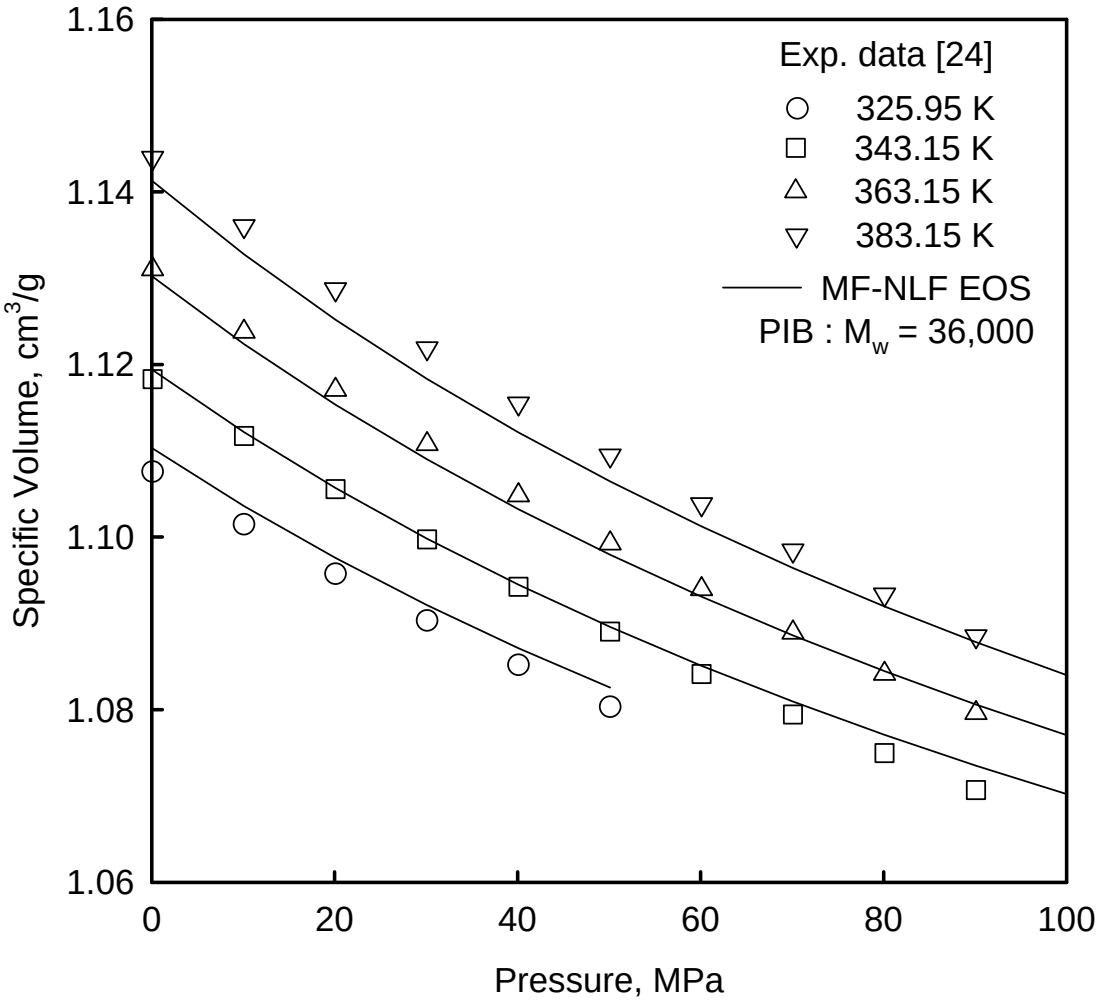


Fig. Calculated and experimental temperature-pressure-volume relations of PIB.

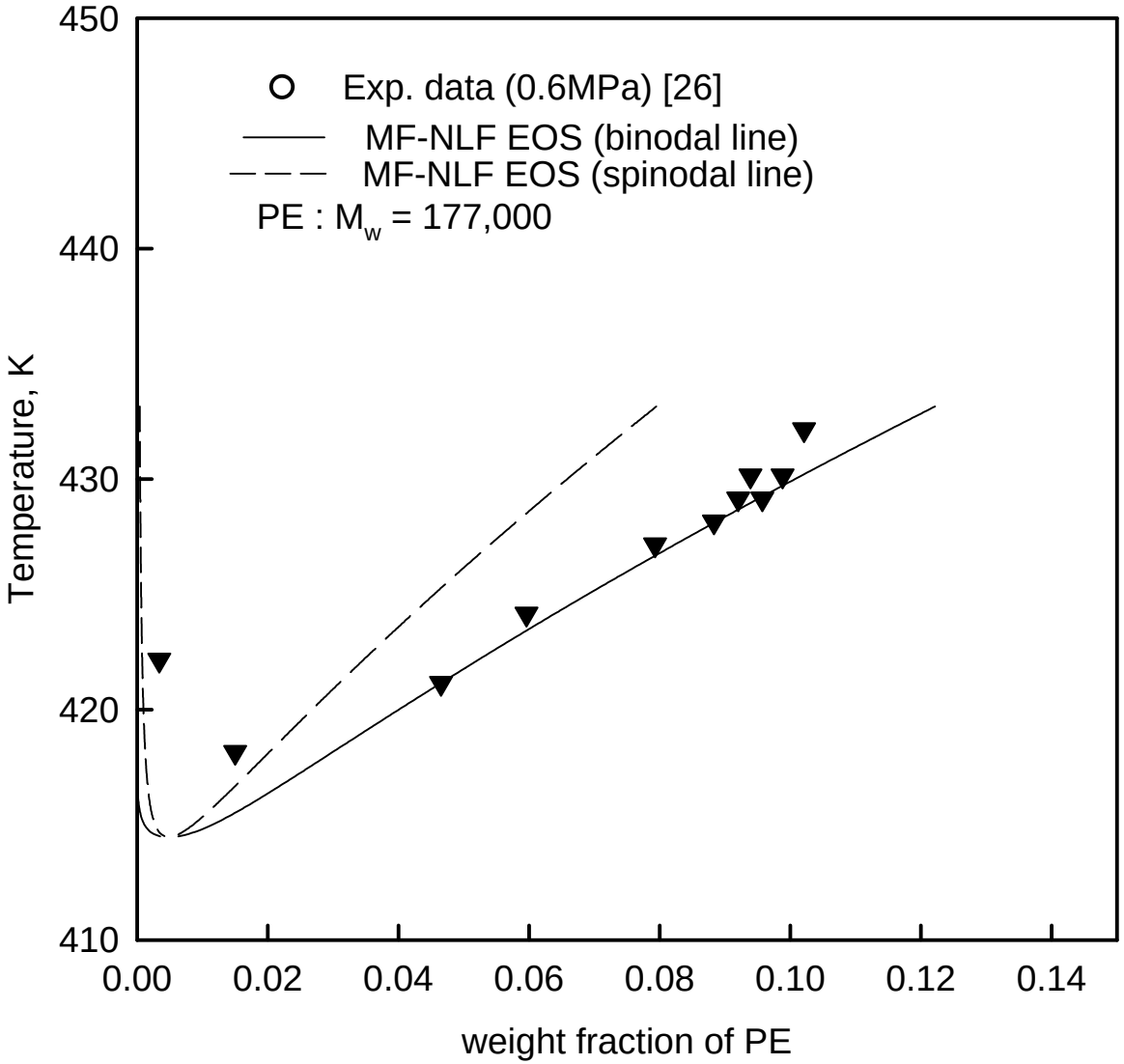


Fig. LLE of PE (Polyethylene)/Hexane solution.

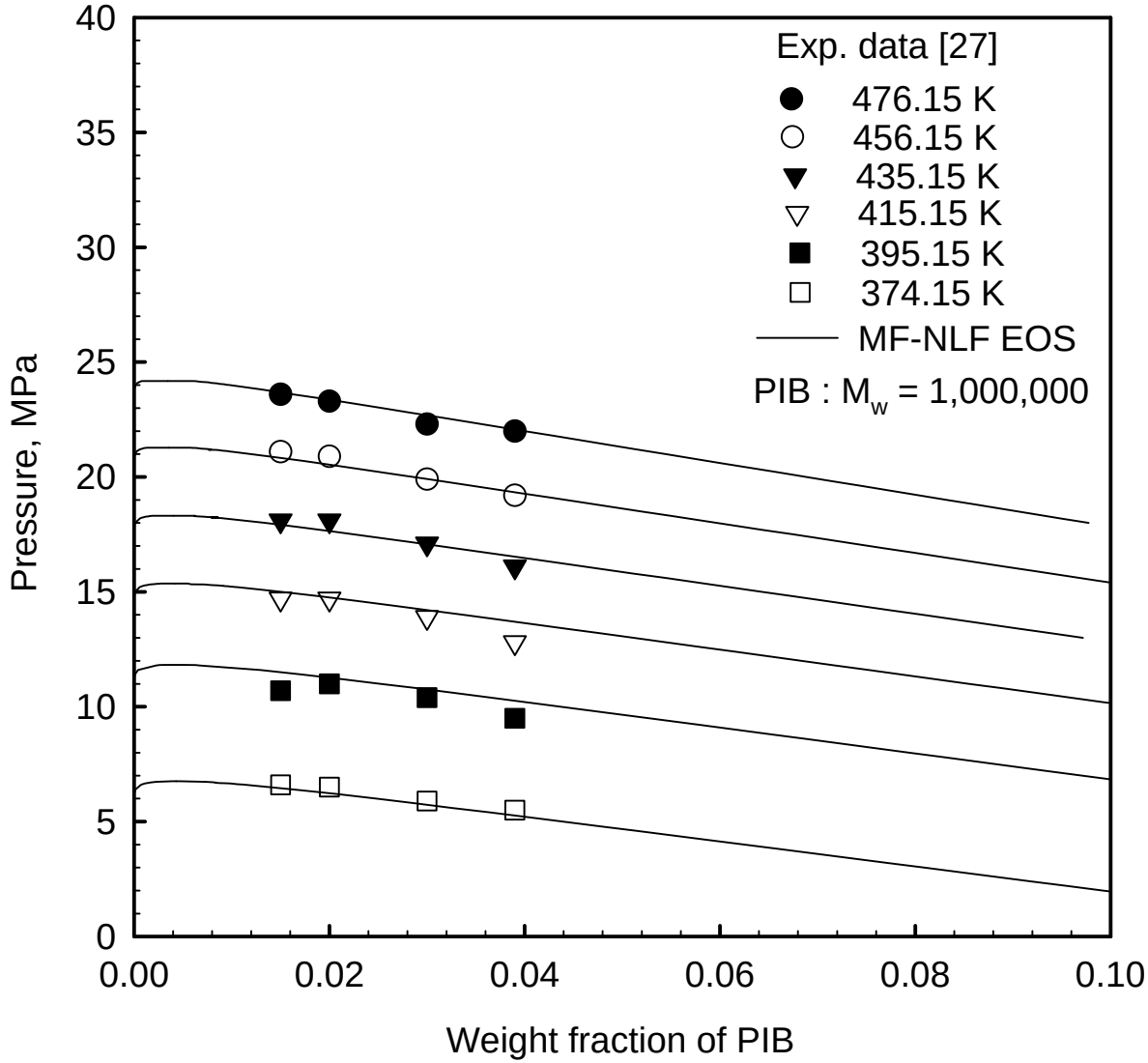


Fig. LLE of PIB (Polyisobutylene)/n-Pentane System.

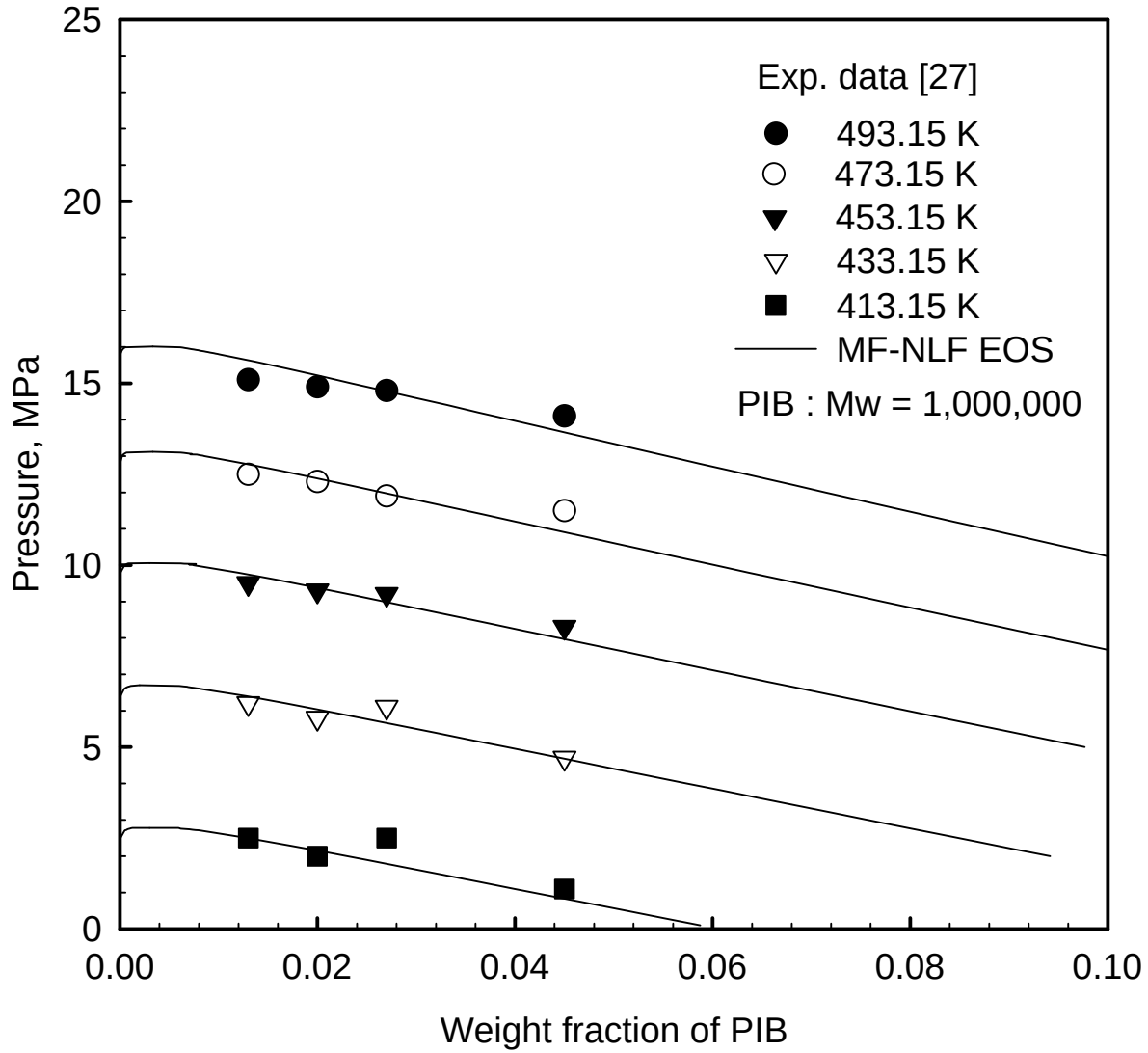


Fig. LLE of PIB (Polyisobutylene)/n-Hexane System.

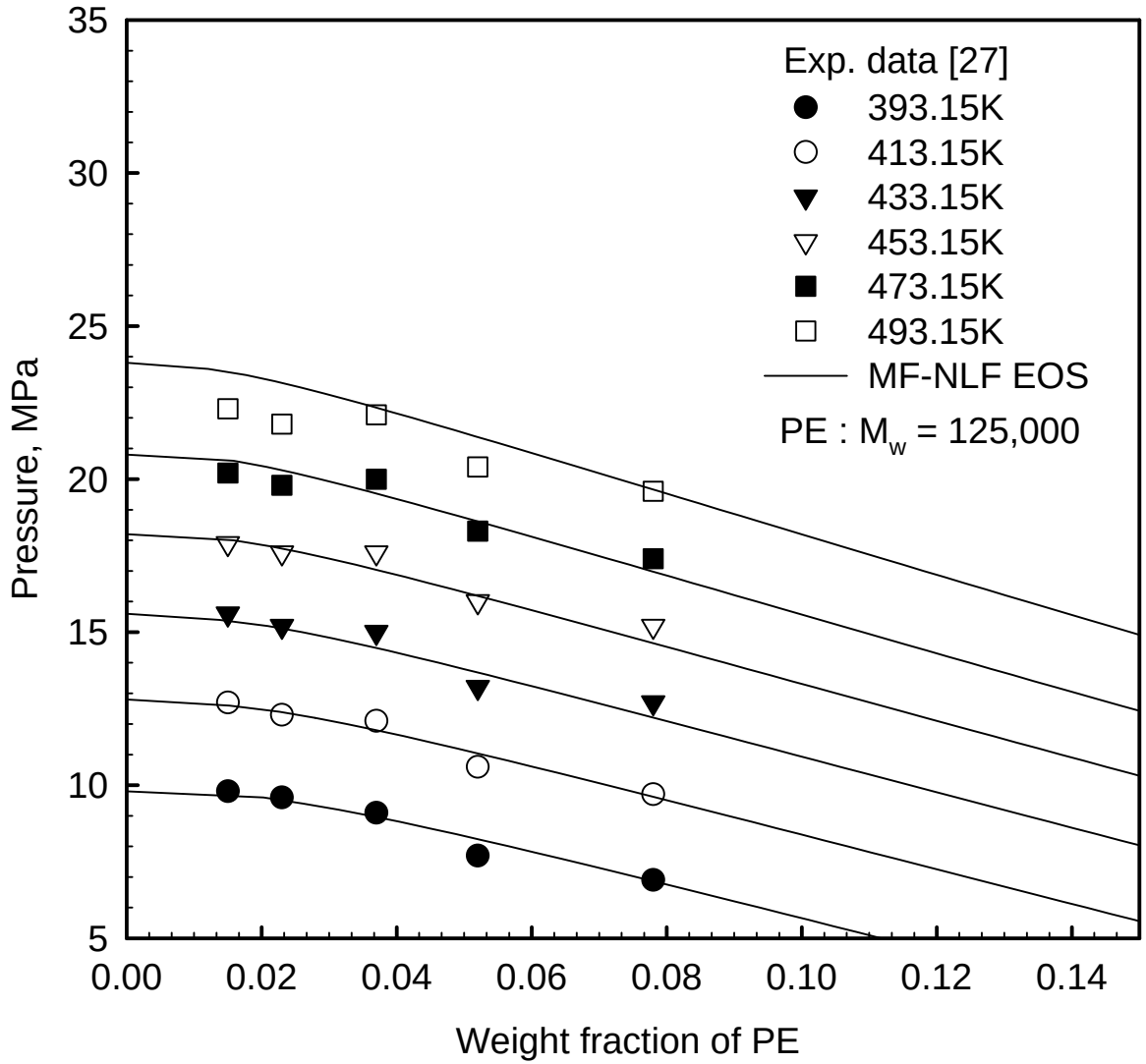


Fig. LLE of PE (Polyethylene)/n-Pentane.

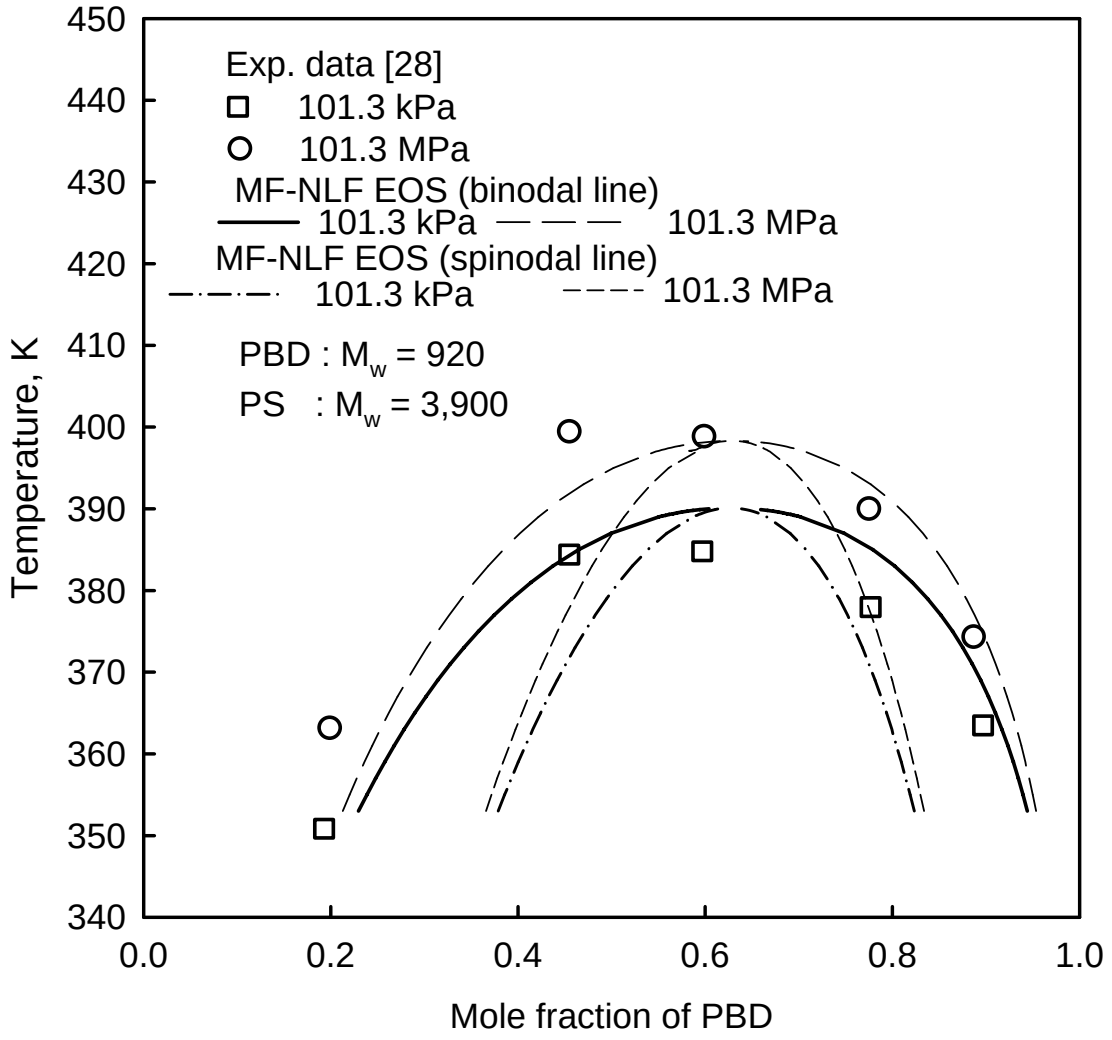


Fig. LLE of PBD (polybutadiene)/PS(Polystyrene) blend.

High Pressure VLE

-water + hydrocarbon systems (near critical region)
-critical loci

Pure Parameter Estimation

- **Previous Method**

Pure component below its critical point

➔ ***Liquid densities and vapor pressures were used for each Isotherm***

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

- **New Method**

(1) Determined volume parameter at its critical point

$$\left(\frac{\partial P}{\partial \rho}\right)_T = 0 \qquad \left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0$$

(2) Energy parameters were obtained from experimental vapor pressure data for each isotherm

$$\varepsilon_{11}/k = E_a + E_b T + E_c T^2$$

Table. Size and energy parameters of the MF-NLF-HB EOS

Substance	V*	E_a (K)	E_b (-)	E_c ×10^7 (K^{-1})
water	23.07	150.9	-0.02007	-736.0
heptane	141.4	83.07	0.02899	-7.088
decane	190.5	83.73	0.04303	-117.7
dodecane	219.5	83.46	0.04705	-103.7
benzene	94.78	97.56	0.03775	-246.4
toluene	112.2	97.81	0.03291	-130.7
p-xylene	129.8	95.54	0.03879	-145.1
ethylbenzene	127.4	97.86	0.03018	-50.78

$$\varepsilon_{11}/k = E_a + E_b T + E_c T^2$$

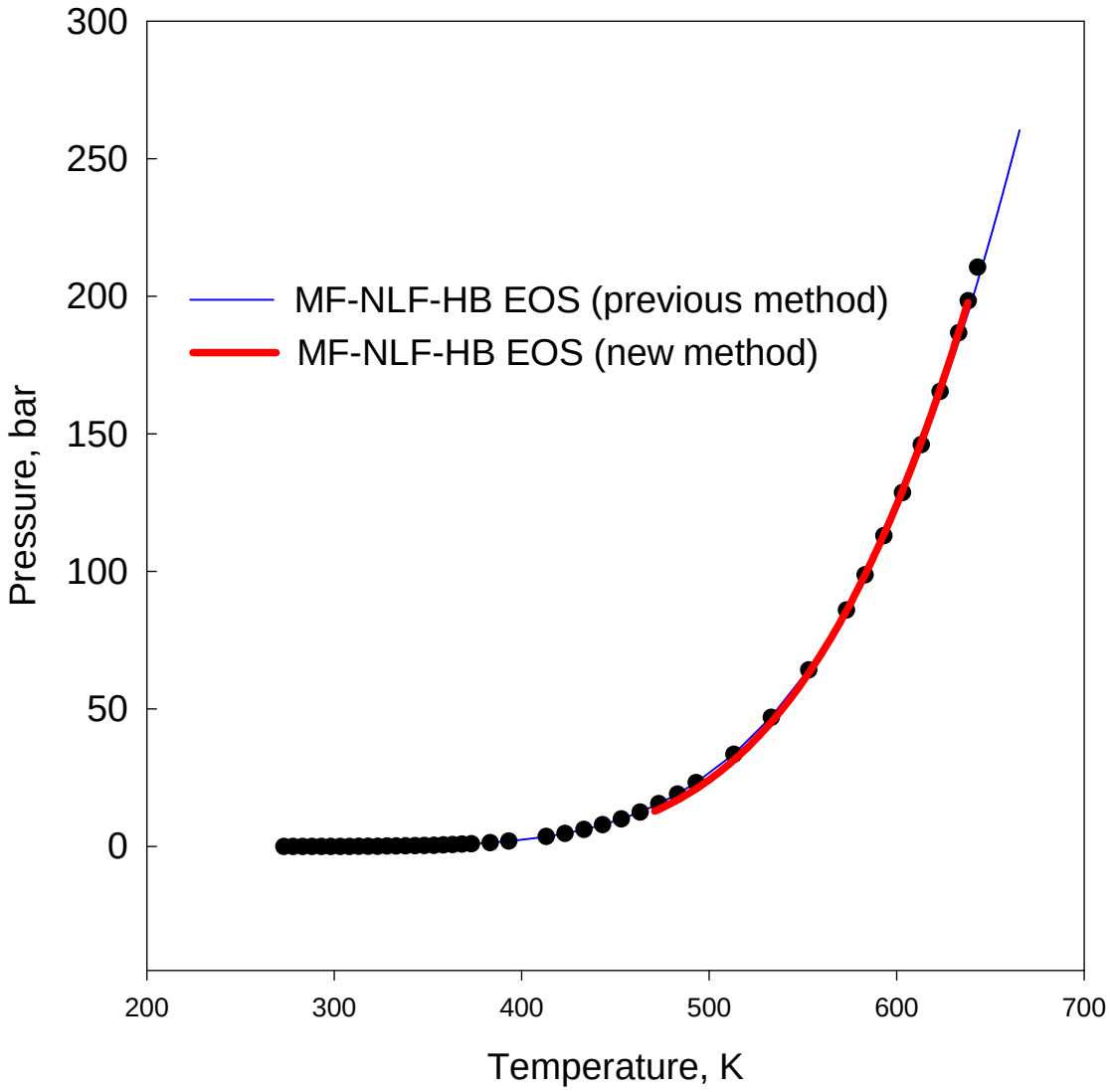


Fig. Vapor Pressure of water

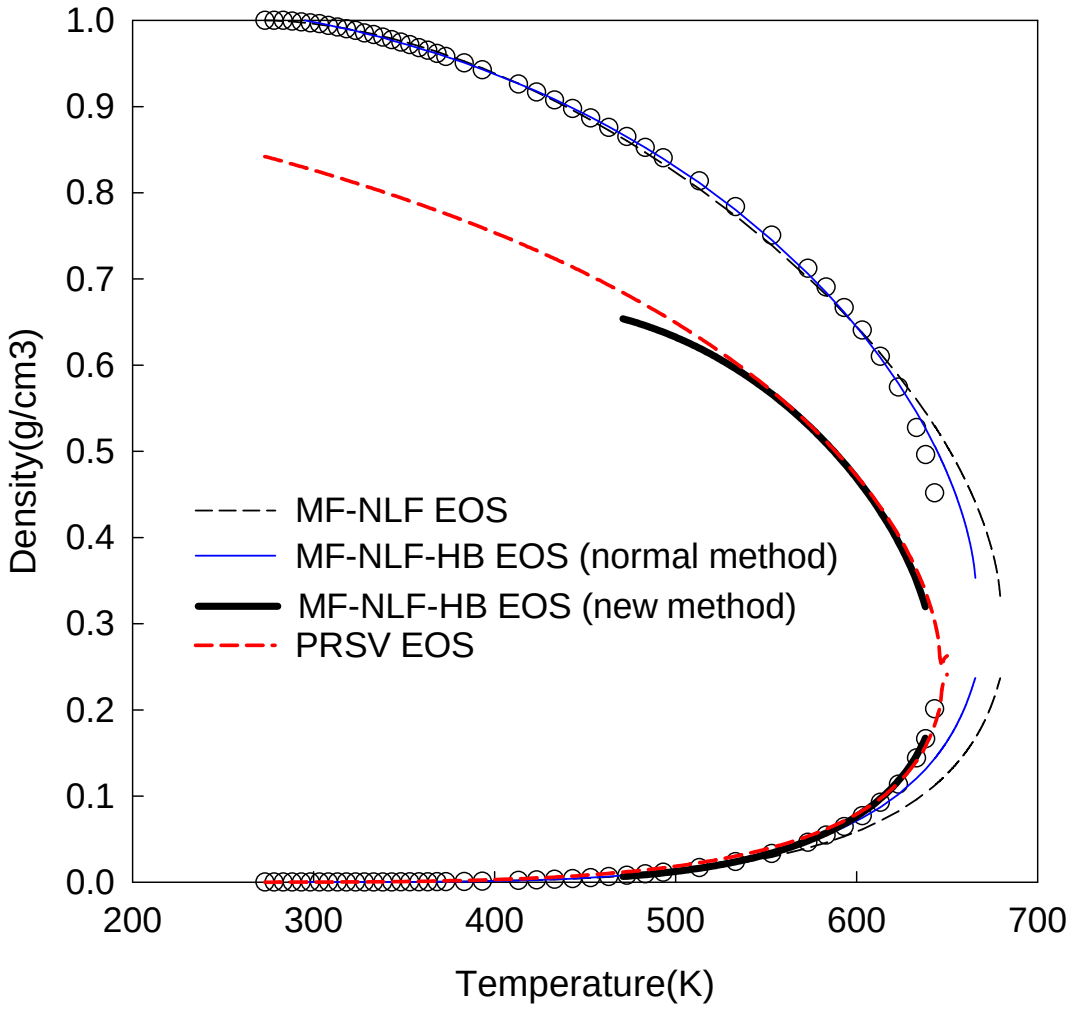
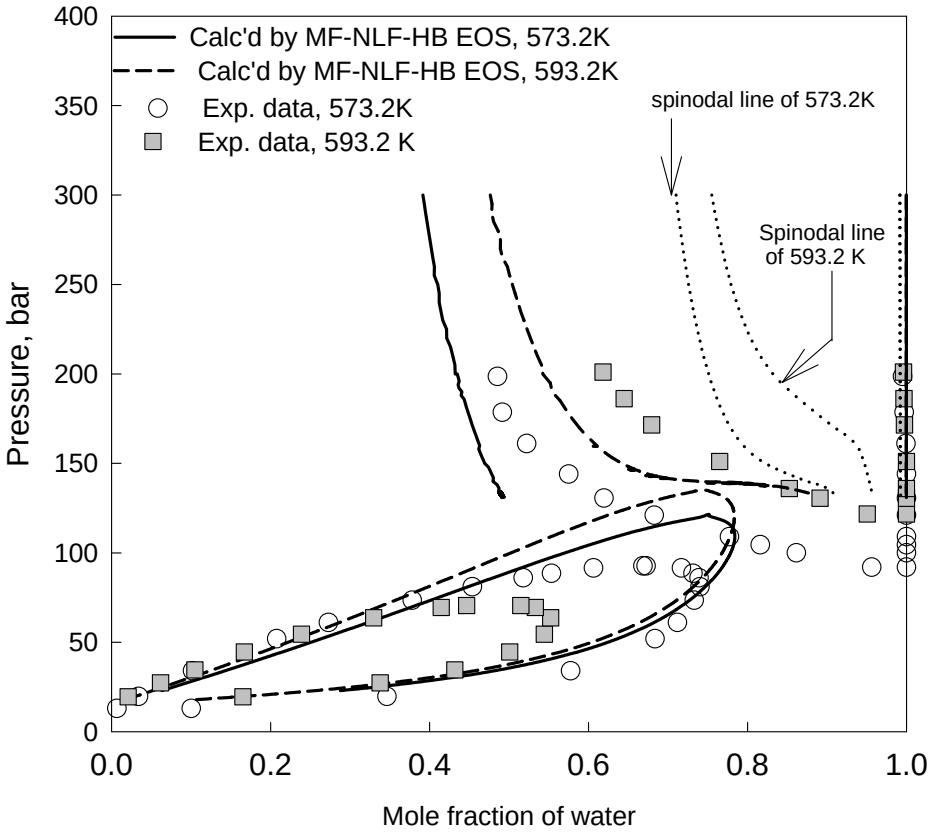
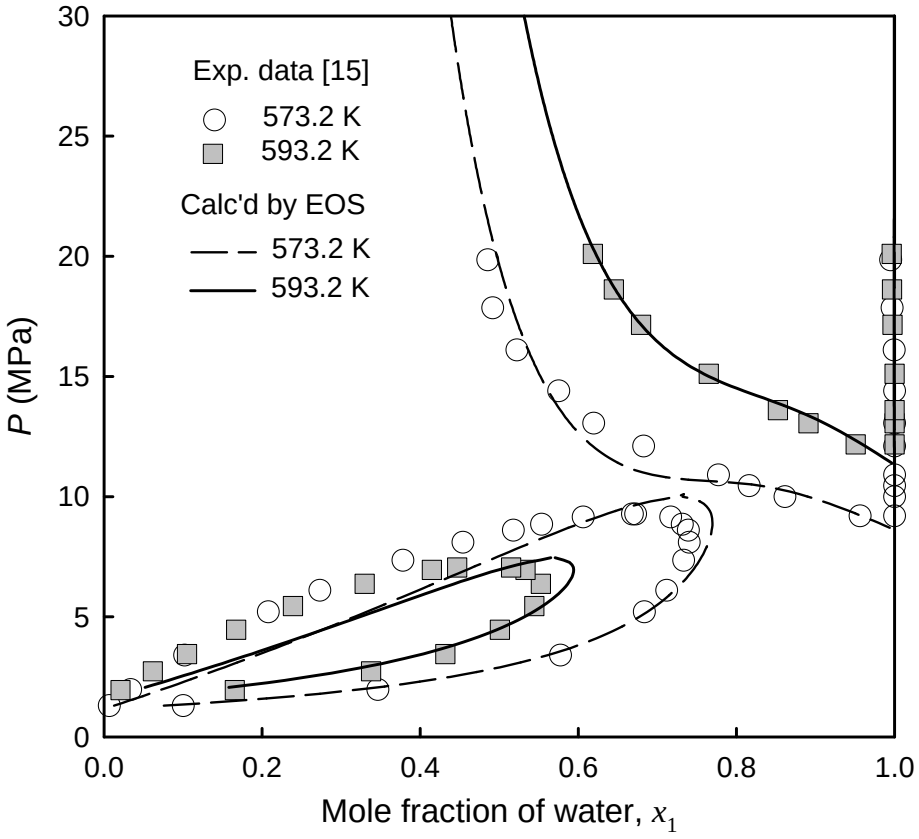


Fig. Saturated density of water





$$r_i = r_a + r_b(T - T_0) + r_c[T\ln(T_0/T) + T - T_0]$$

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

V*

$$\varepsilon_{11}/k = E_a + E_bT + E_cT^2$$

Fig. Phase behavior of water + decane system

물+탄화수소계
상거동

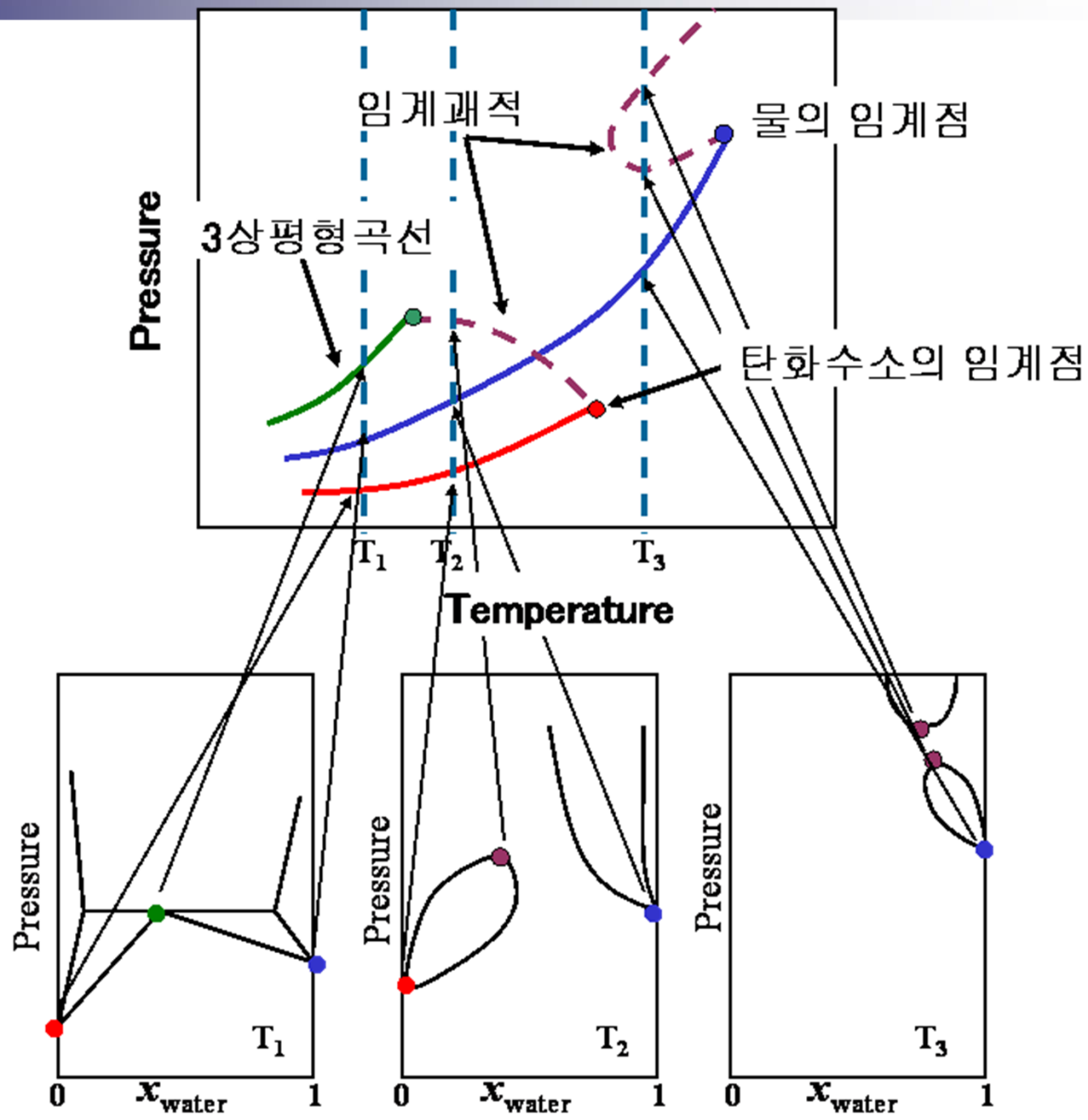

임계괘적
물의 임계점
3상평형곡선
탄화수소의 임계점
Pressure
T_1
T_2
T_3
Temperature
Pressure
T_1
0
x_{water}
1
Pressure
T_2
0
x_{water}
1
Pressure
T_3
0
x_{water}
1

Table. Binary parameters and average deviation for the MF-NLF-HB EOS

System (1) + (2)	T (K)	k_{12}	vapor-liquid		fluid I-fluid II	
			[a] $\Delta X \cdot 10^2$	[b] $\Delta Y \cdot 10^2$	[c] $\Delta X^{I} \cdot 10^2$	[d] $\Delta X^{II} \cdot 10^2$
water + decane	573.2	0.231	7.11	2.26	0.0895	2.81
	593.2	0.222	7.47	1.77	0.136	0.961
water + dodecane	603.6	0.213	7.59	1.75	2.42	4.03
	633.2	0.210	8.82	1.61	5.01	1.82
water + heptane	623.2	0.117	-	-	0.233	-
	628.2	0.102	6.87	1.23	2.304	1.40
water + benzene	553.2	0.045	-	-	0.888	1.27
	579.2	0.030	-	-	1.91	0.793
	603.2	0.053	-	-	3.70	1.37
water + toluene	553.2	0.088	-	-	0.306	0.626
	573.2	0.078	-	-	0.450	1.11
	583.2	0.060	-	-	0.379	0.906
water + ethylbenzene	553.2	0.107	-	-	0.150	0.924
	583.2	0.093	-	-	0.662	1.51
water + *p*-xylene	553.2	0.119	-	-	0.248	0.936
	583.2	0.097	-	-	0.459	1.19

$$\Delta X = \left| x_i^{cal} - x_i^{exp} \right| / n \qquad \Delta Y = \left| y_i^{cal} - y_i^{exp} \right| / n$$

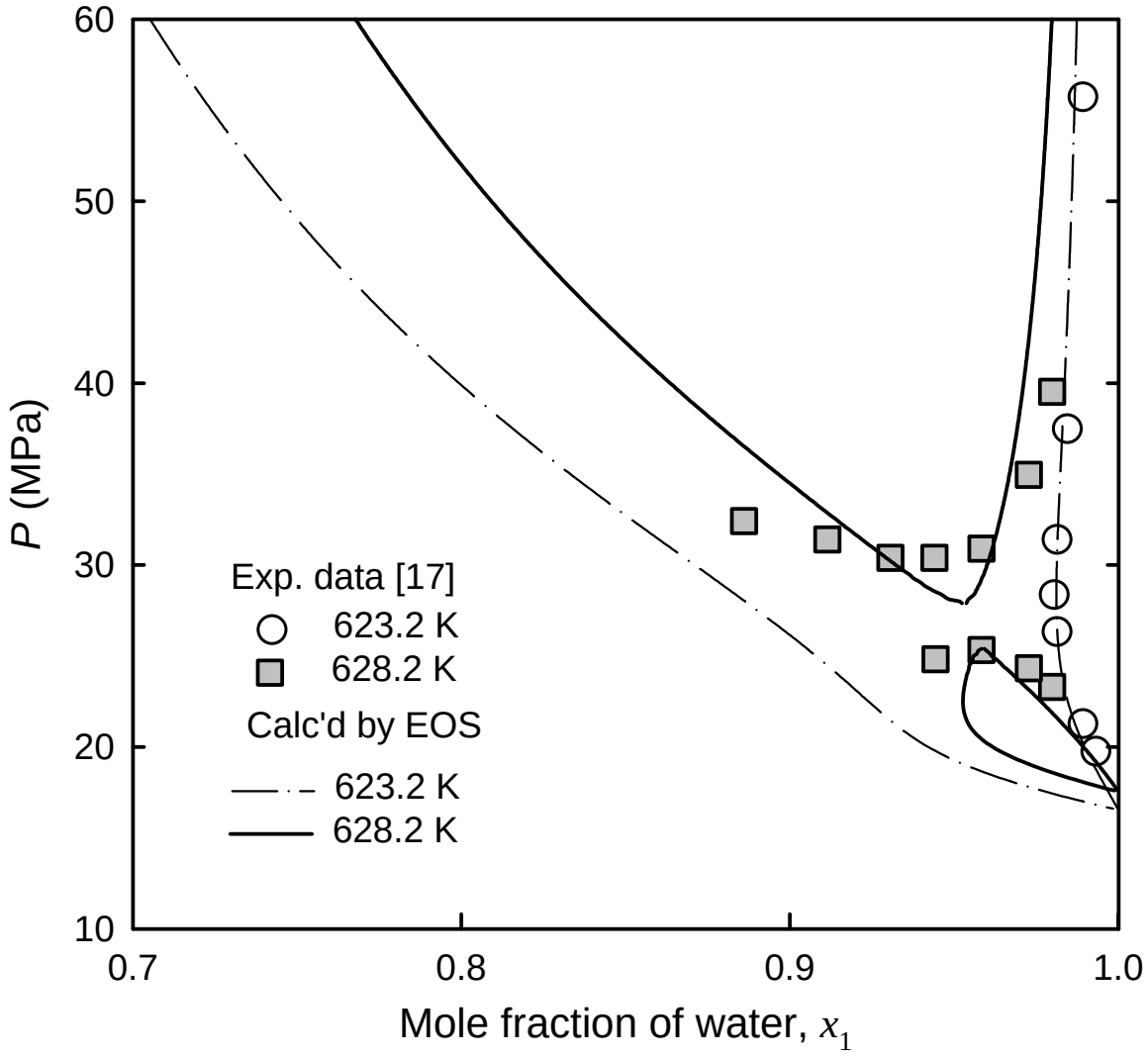


Fig. Phase behavior of water + heptane system

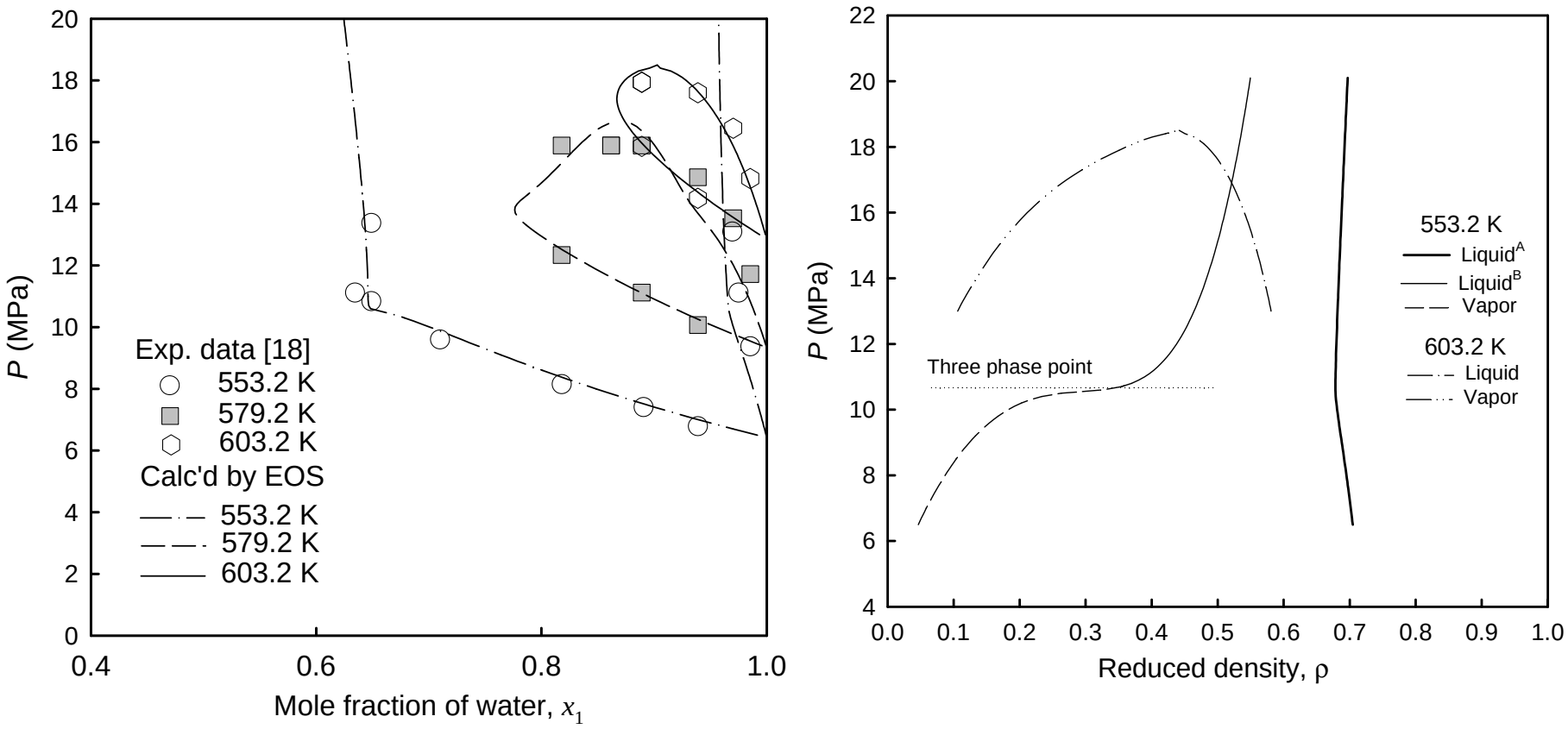


Fig. Phase behavior of water + benzene system

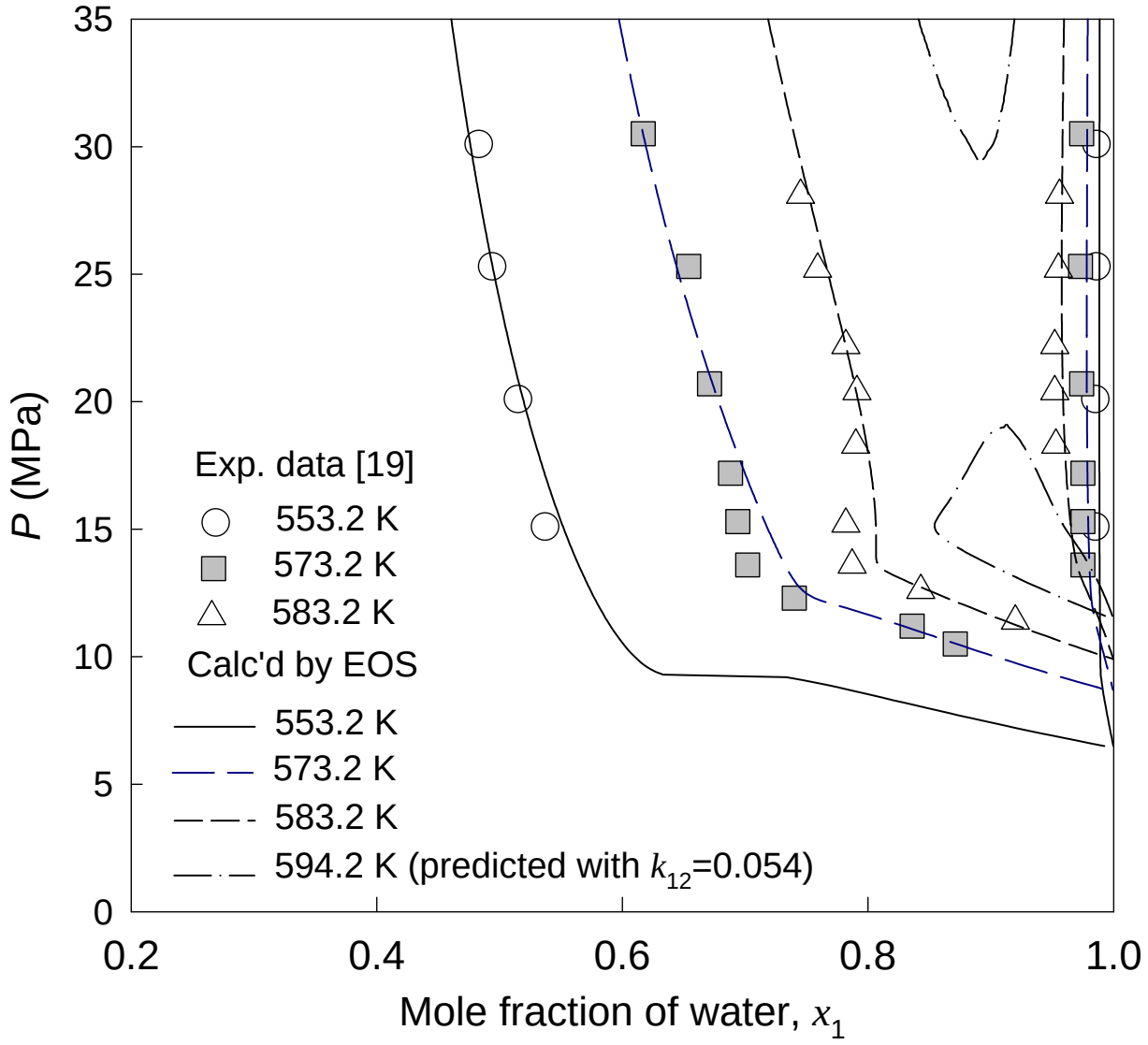


Fig. Phase behavior of water + toluene system

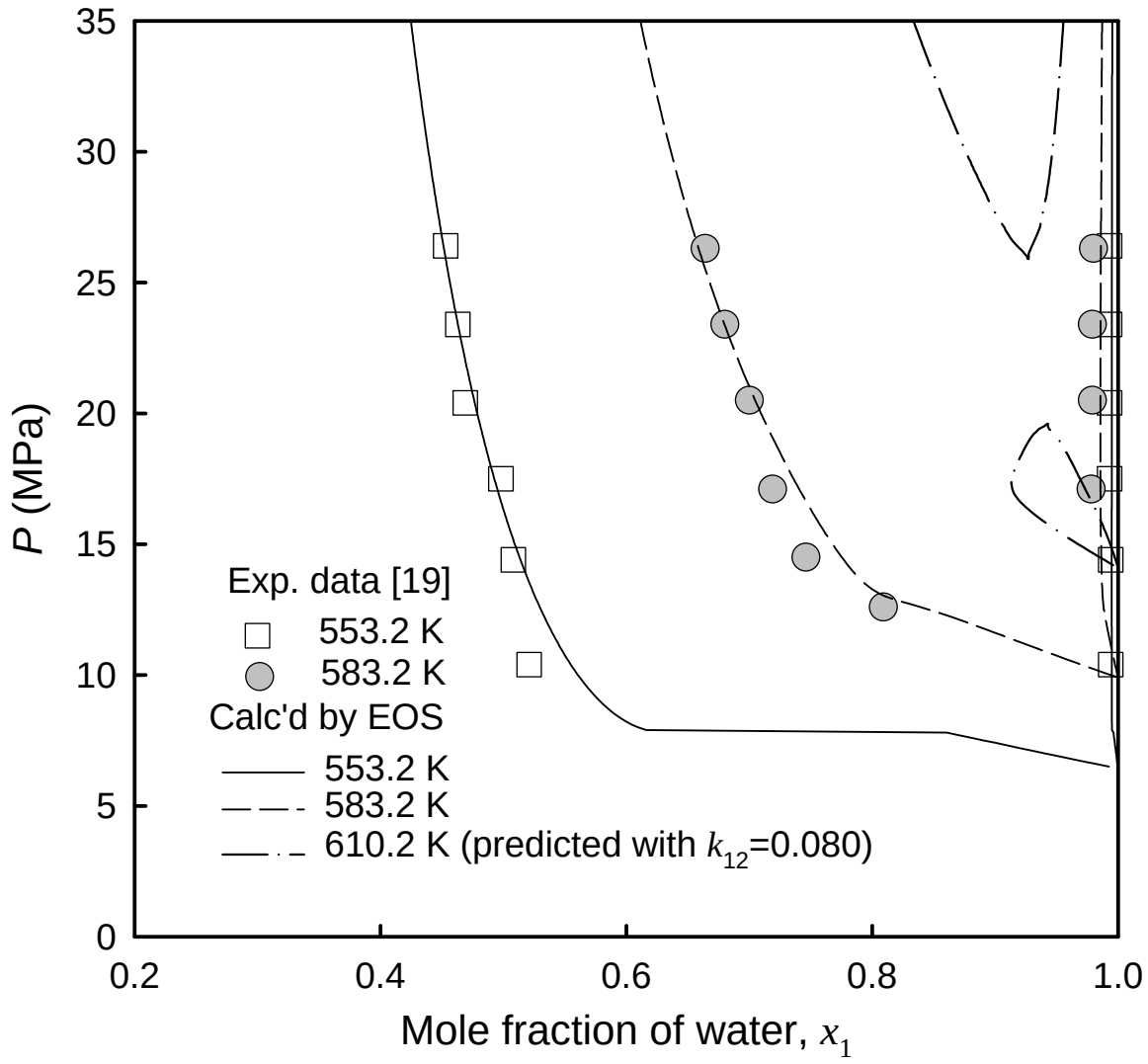


Fig. Phase behavior of water + ethylbenzene system

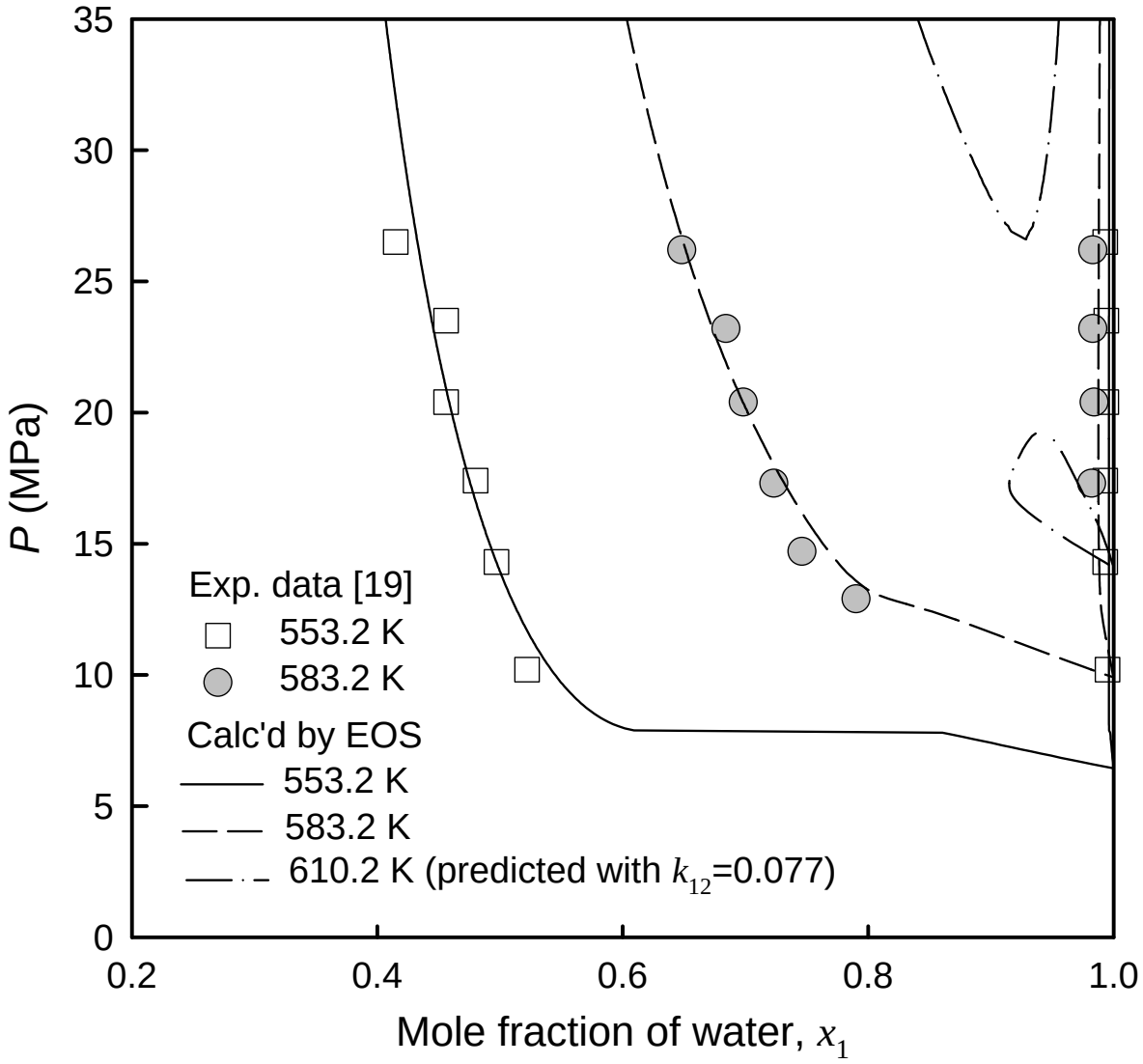


Fig. Phase behavior of water + *p*–xylene system

Critical Loci of water + hydrocarbon system

Binary Interaction Parameters of MF-NLF EoS

Substance	Binary parameter (k_{ij})	Type of critical loci
Water + heptane	0.25	Type III
Water + decane	0.24	Type III
Water + hexadecane	0.24	Type III
Water + benzene	0.25	Type III
Water + toluene	0.21	Type III
Water + ethylbenzene	0.22	Type III
Water + tetralin	0.23	Type II
Water + methylnaphthalene	0.22	Type II

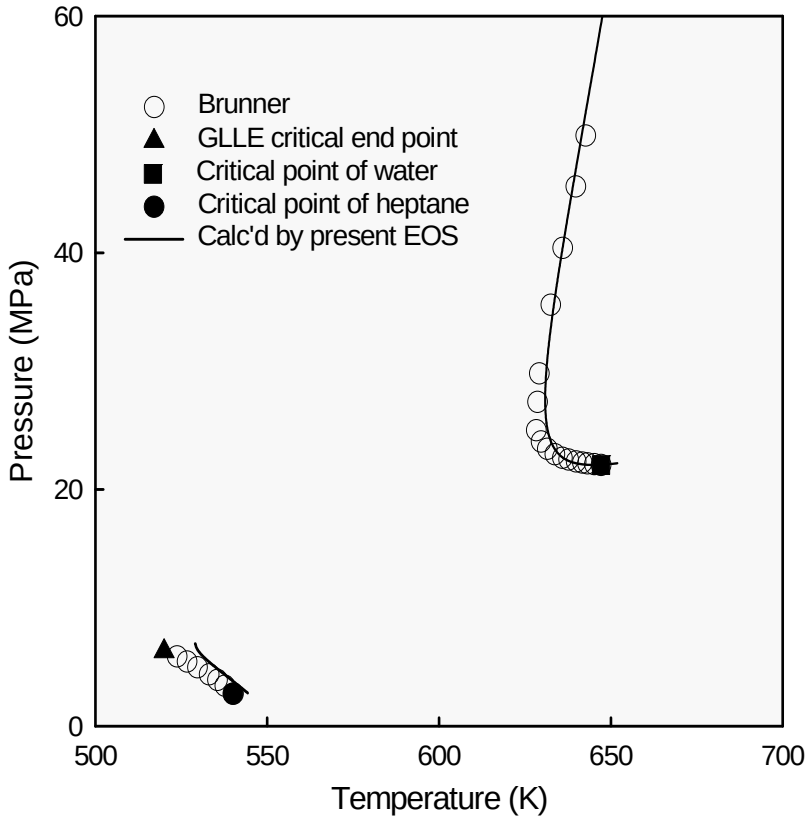


Fig. Critical loci of water + heptane system (k_{ij} = 0.25)

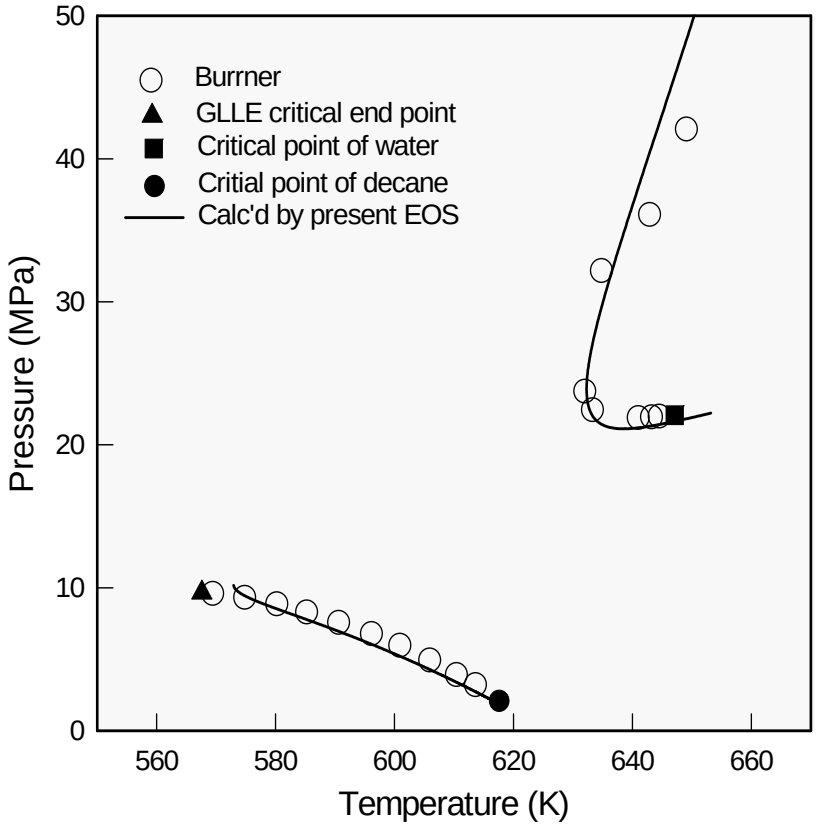


Fig. Critical loci of water + decane system (k_{ij}= 0.24)

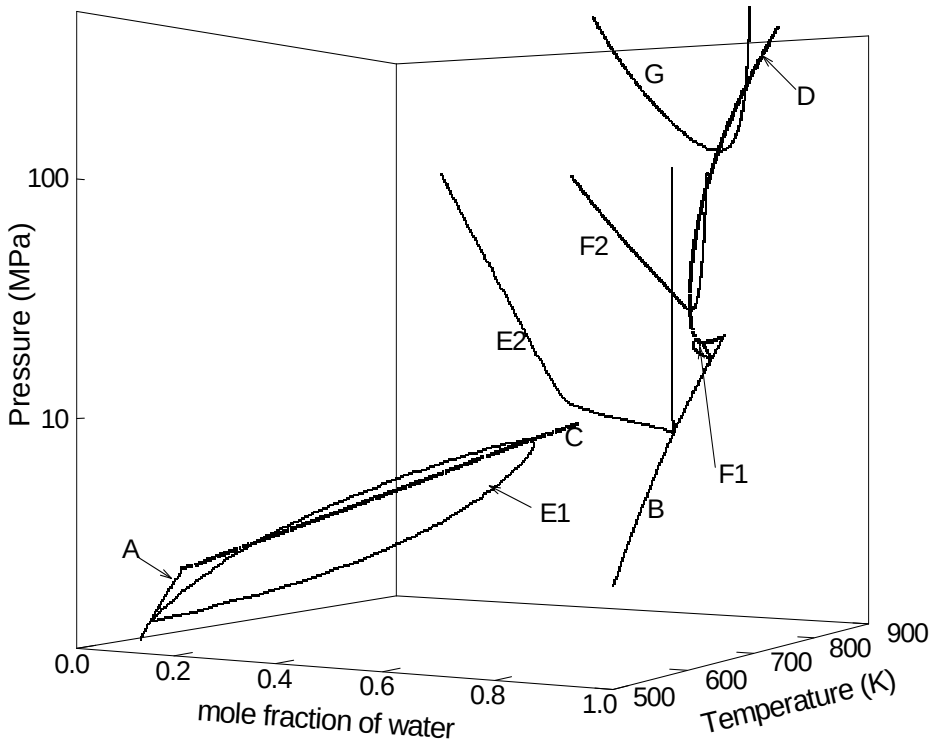


Fig. Three dimensional phase diagram of water+decane system.

A: vapor pressure of decane; B: vapor pressure of water; C, D : critical loci; E1 : gas-liquid equilibria at 580 K; E2 : gas-liquid and liquid-liquid equilibria at 580 K; F1: gas-liquid equilibria at 634 K; F2 : liquid-liquid equilibria at 634 K; G: liquid-liquid equilibria at 700 K

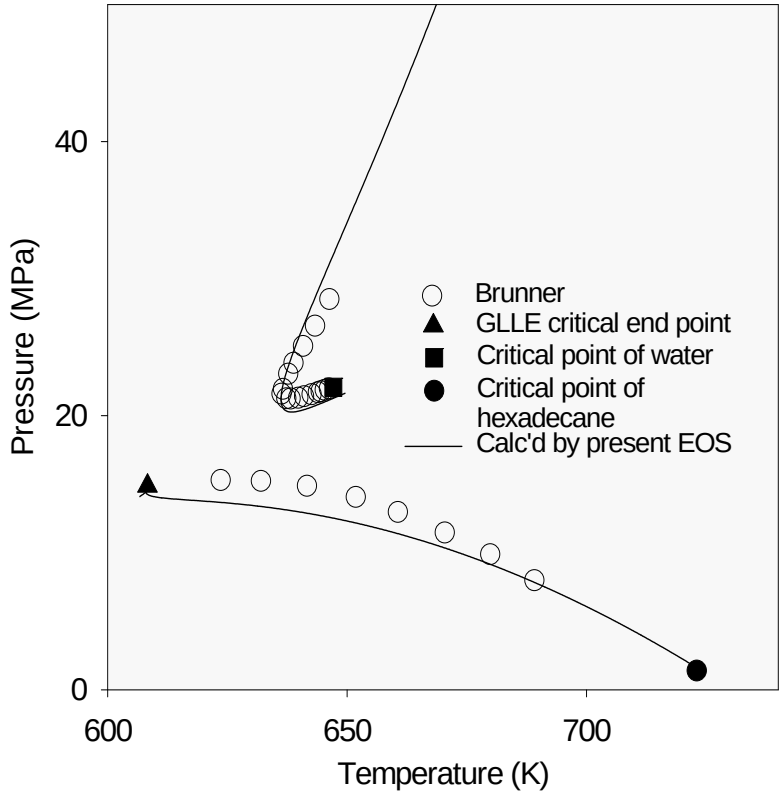


Fig. Critical loci of water + hexadecane system (k_{ij}= 0.24)

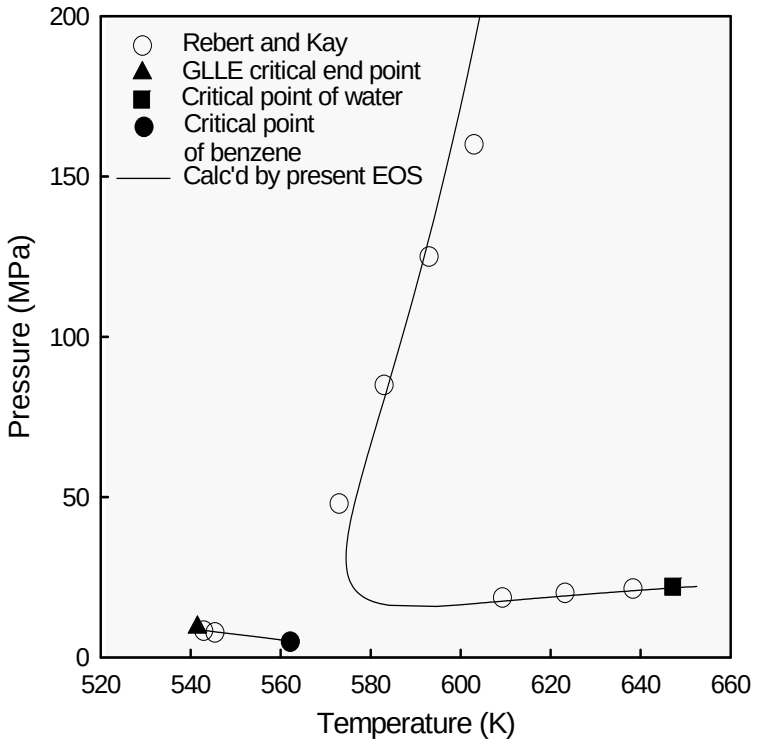


Fig. Critical loci of water + benzene system (k_{ij}= 0.25)

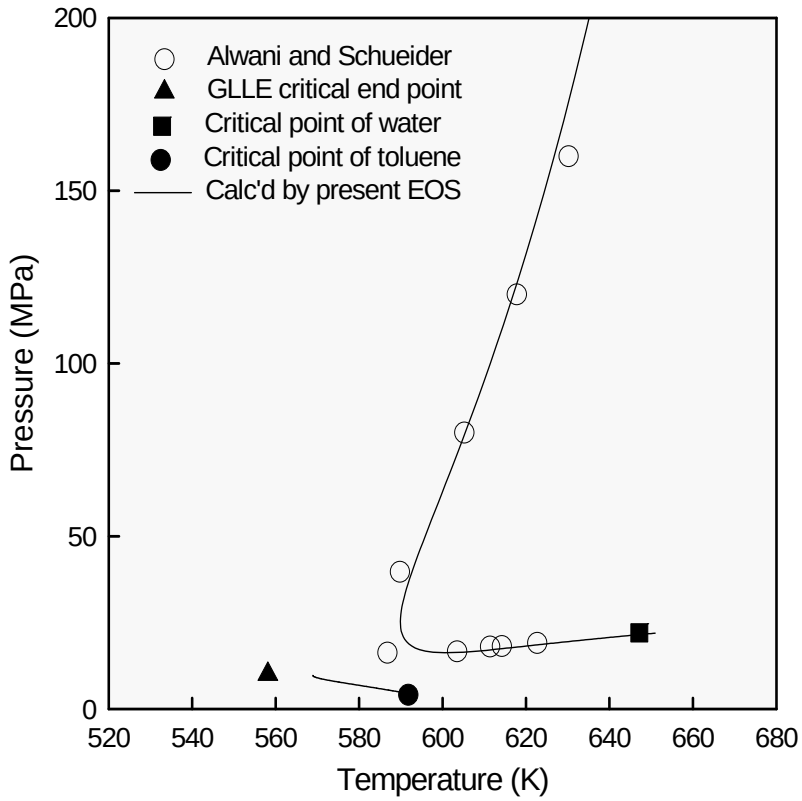


Fig. Critical loci of water + toluene system (k_{ij}= 0.21)

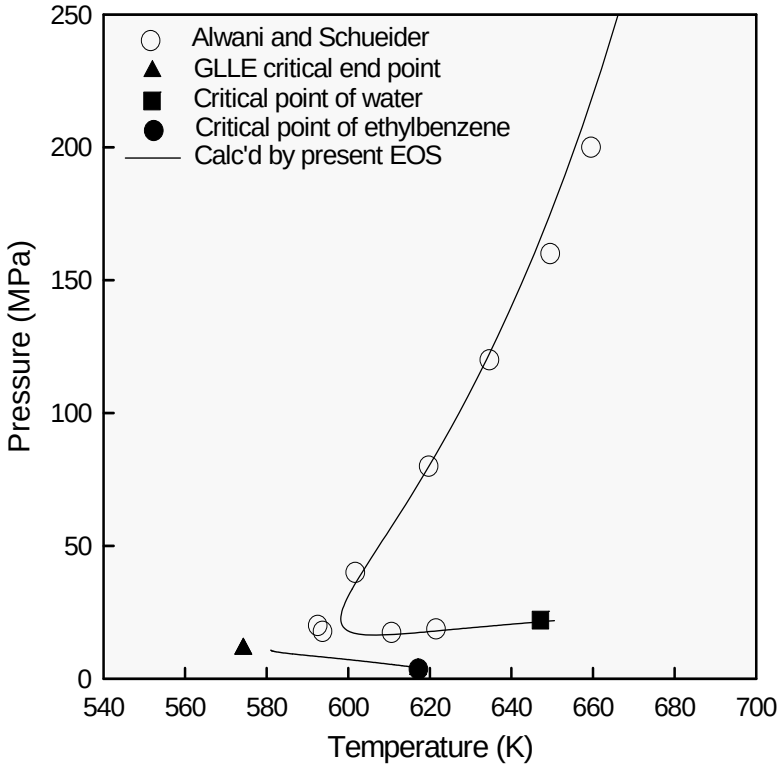


Fig.. Critical loci of water + ethylbenzene system (k_{ij}= 0.22)

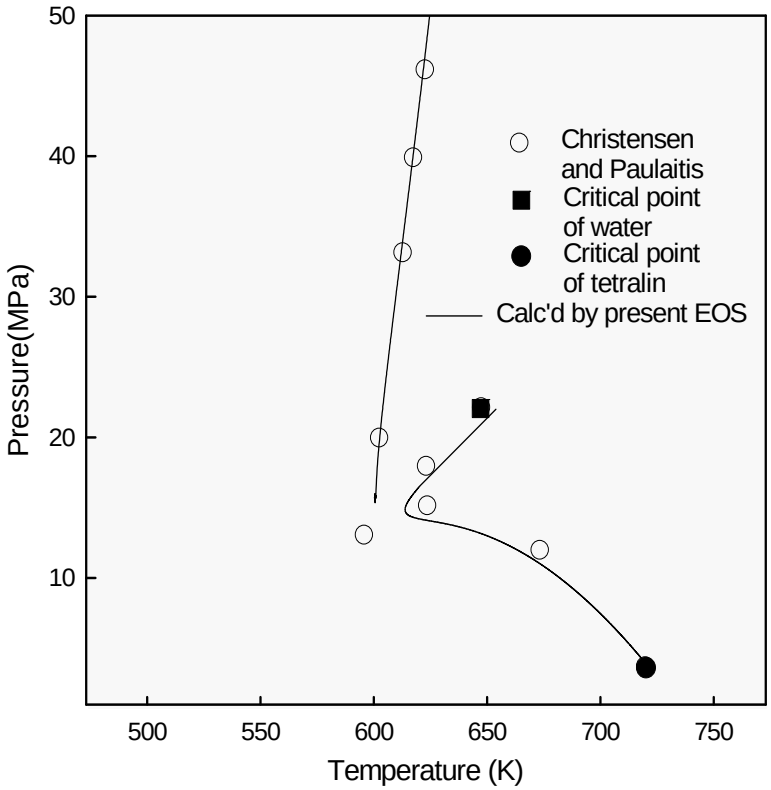


Fig. Critical loci of water + tetralin system (k_{ij}= 0.23)

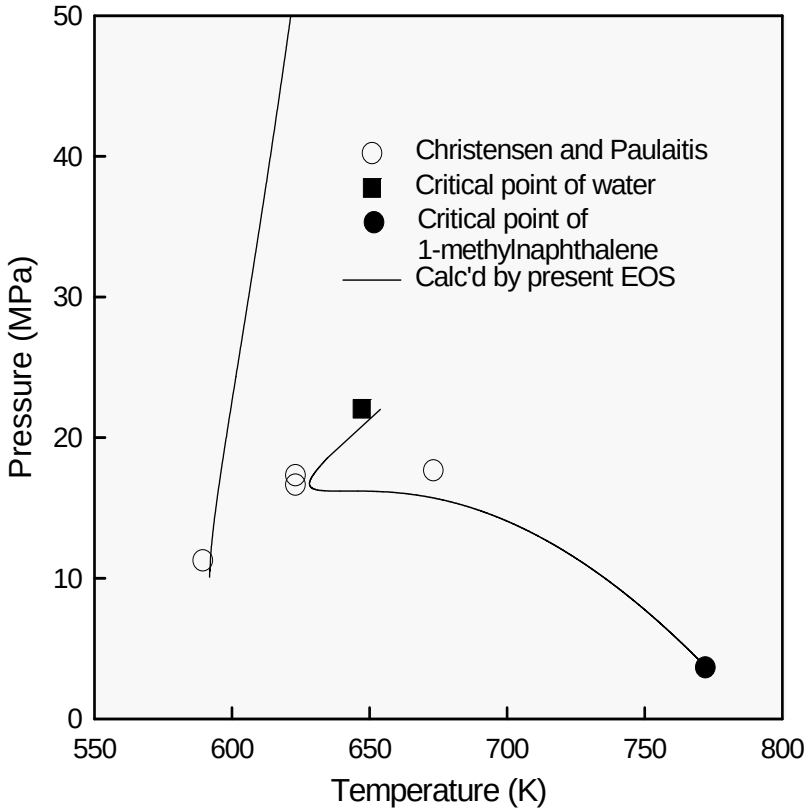


Fig. Critical loci of water + 1-methylnaphthalene system (k_{ij}= 0.22)

Concluding Remarks

◆ Good results for high pressure LLE of polymer solutions were obtained

◆ New pure parameter estimation method was applied for near critical VLE of water + hydrocarbon systems