A Review on Equations of State Applicable to Polymers and Complex Systems

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Motivation

❑ **Increasing demands of EOS models for various process conditions and complex systems**

- *Supercritical conditions and high pressure systems*
- *Phase equilibria of polymers*
- *Phase equilibria of associating mixtures (alcohols, acids)*
- *Simultaneous representation of VLE and* H^E

❑ **EOS approach provides integrated approach covering wider range of process conditions and various properties**

❑ **Characteristics and understanding of each EOS models are important for various applications.**

Three Classes of EOS Models

❑ Based on Semi-Classical Partition Function

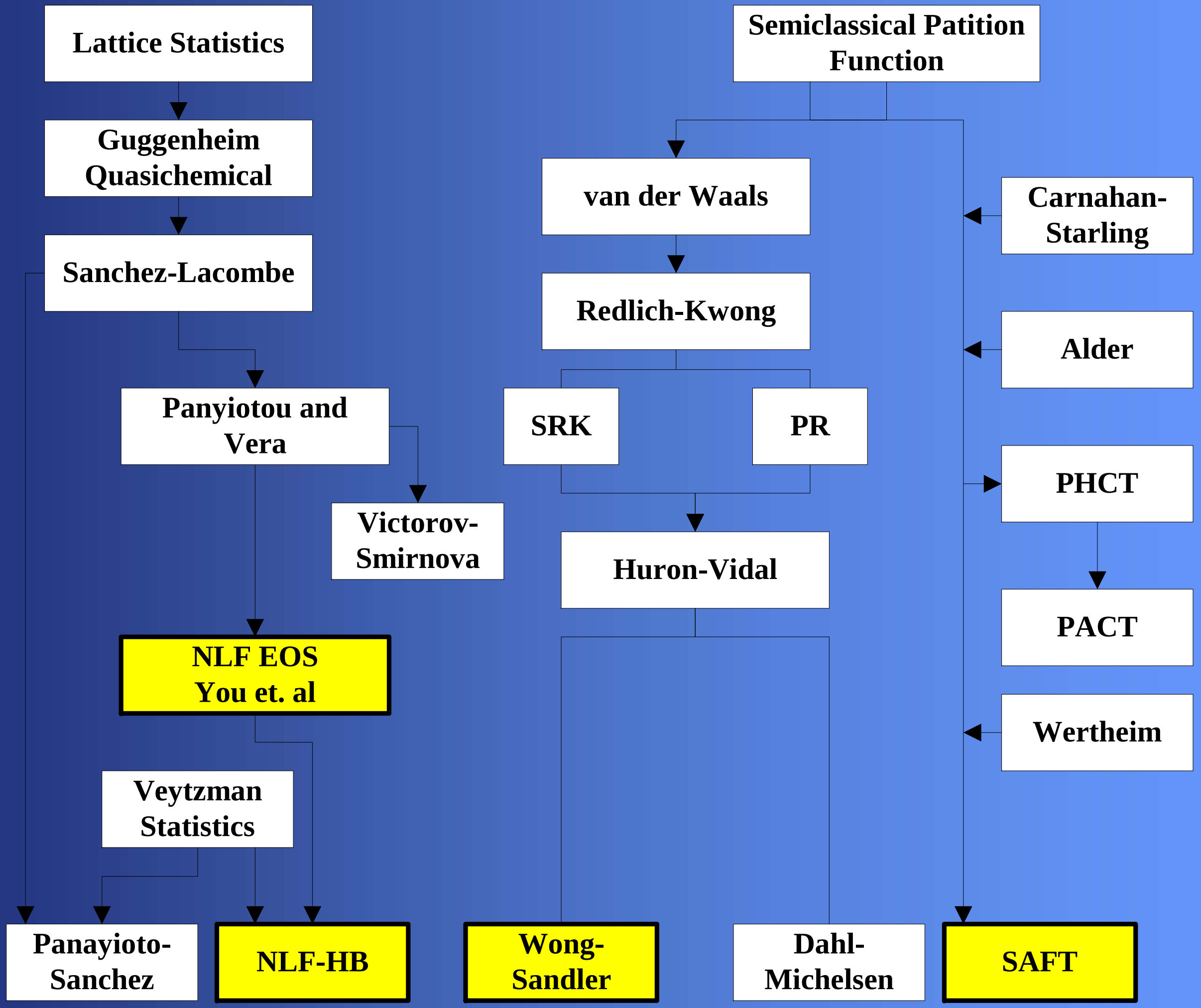
- *Cubic Equation of State and Other van-der Waals based EOS*
  - *Soave-Redlich-Kwong (1972), Peng-Robinson EOS (1976)*
  - *Mixing Rules proposed by Huron-Vidal (1979) , Michelsen (1990) and Wong-Sandler (1992)*

- *Radial Distribution Function Approaches*
  - *PHCT (1978), PACT (1985)*
  - *SAFT (Huang and Radosz, Chapman, 1990)*

❑ Based on Lattice Statistics

- *Sanchez-Lacomb (1976)*
- *Panayiotou-Vera (1981)*
- *NLF -EOS proposed by You,Yoo and Lee (1993)*
- *Hydrogen Boding proposed by Veytzman (1990) + Lattice EOS*
  - *Panayiotou-Sanchez (1991), NLF-HB EOS (Yeom et. al., 1999)*

Three Classes of EOS Models – Historical Review



Lattice Statistics

Guggenheim Quasichemical

Sanchez-Lacombe

Panyiotou and Vera

Victorov-Smirnova

NLF EOS You et. al

Veytzman Statistics

Panayioto-Sanchez

NLF-HB

Semiclassical Patition Function

van der Waals

Redlich-Kwong

SRK

PR

Huron-Vidal

Wong-Sandler

Dahl-Michelsen

Carnahan-Starling

Alder

PHCT

PACT

Wertheim

SAFT

EOS Models Selected for Comparison

- ❑ **Peng-Robinson Equation of State with Wong-Sandler Mixing Rule (PR-WS)**
  - *Peng and Robinson (1976) : EOS*
  - *Wong and Sandler (1992) : Mixing Rule*
  - *Mathias and Copeman (1983) : a(T) law*
- ❑ **Statistically Associated Fluid Model (SAFT)**
  - *Huang and Radosz, Chapman (1990)*
- ❑ **Nonrandom Lattice Fluid EOS with Hydrogen Bonding (NFL-HB)**
  - *You, Yoo and Lee (1993)*
  - *Yeom, Yoo and Lee (1999)*

Comparison

- Number of pure and mixture parameters
- Procedure to obtain pure component parameters and binary interaction parameters

- Pure component properties (vapor pressure and liquid density)
- Binary VLE calculation of various mixtures
- Polymer solubility calculation

- Computation time
- Sensitivity of VLE calculation with respect to binary interaction parameters (robustness)

Peng-Robinson EOS with Wong-Sanler Mixing Rule (PR-WS EOS)

EOS

$$Z = \frac{V}{V-b} - \frac{a(T)V}{RT(V+\varepsilon b)(V+\sigma b)}$$

Generalized form of Cubic EOS

a(T) law

$$a(T) = a_c \alpha(T)$$

$$\alpha = [1 + C_1(1-T_R^{0.5}) + C_2(1-T_R^{0.5})^2 + C_3(1-T_R^{0.5})^3]^2$$

Mathias-Copeman a(T) law (1983)

Mixing Rule

Wong-Sanldler mixing rule (1992)

$$G^{ex}(T, P = 1\,\text{bar}, x_i) \approx A^{ex}(T, P = 1\,\text{bar}, x_i) \approx A^{ex}(T, \text{high P}, x_i)$$

$$B(x_i, T) = \sum\sum x_i x_j B_{ij}(T) = \sum\sum x_i x_j \left(b_{ij} - \frac{a_{ij}}{RT} \right) = b - \frac{a}{RT}$$

$$b_{ij} - \frac{a_{ij}}{RT} = \frac{1}{2}\left[\left(b_{ii} - \frac{a_{ii}}{RT} \right) + \left(b_{jj} - \frac{a_{jj}}{RT} \right) \right](1 - k_{ij})$$

Statistical Associating Fluid Theory (SAFT)

EOS

$$Z = 1 + Z_{hs} + Z_{chain} + Z_{disp} + Z_{assoc}$$

Carnahan and Starling (1969)

Hard Sphere Term

$$Z_{hs} = \frac{6}{\pi N_A \rho}\left[\frac{\xi_0\xi_3}{1-\xi_3} + \frac{3\xi_1\xi_2}{(1-\xi_3)^2} + \frac{(3-\xi_3)\xi_2^3}{(1-\xi_3)^3}\right] \qquad \xi_k = (\pi N_A \rho / 6)\sum_i x_i r_i (d_i)^k$$

Chapman (1990)

Chain Term

$$Z_{chain} = \sum_i x_i (1-r_i) L(d_i) \qquad L(d_i) = \frac{2\xi_3 + 3d_i\xi_2 - 4\xi_2^3 + 2d_i\xi_2^2 + 2\xi_3^3 + d_i^2\xi_2^2\xi_3 - 3d_i\xi_2\xi_3^2}{(1-\xi_3)(2-4\xi_3 + 3d_i\xi_2 + 2\xi_3^2 + d_i^2\xi_2^3 - 3d_i\xi_2\xi_3)}$$

Based on Alder (1972)
Chen and Kreglewski (1977)

Dispersion Term

$$Z_{disp} = r\sum_n \sum_m mD_{nm}(u/kT)^n(\xi_3/\xi_{3cp})^m$$

Based on Wertheim (1984)
Chapm;an (1990)

Association Term

$$Z_{assoc} = \rho\sum x_i\left[\sum \left(1/X^{S_i} - 1/2\right)\left(\partial X^{S_i}/\partial\rho\right)\right]$$

$$X^{S_i} = \left(1 + N_A\sum_j \sum_{Y_j} x_j \rho X^{Y_j} W_{ij}\right)^{-1}$$

Nonrandom Lattice Fluid EOS with Hydrogen Bonding (NLF-HB EOS)

EOS

$$Z = 1 + Z_{ath} + Z_{res} + Z_{assoc}$$

You, Yoo and Lee (1993)

Athermal Contribution

$$Z_{ath} = (zN_r / 2N_A)\ln\left[1 + \left(q_M / r_M - 1\right)\rho\right]$$

Residual Contribution

You, Yoo and Lee (1993)

$$Z_{res} = (zN_r / 2N_A)\theta^2 \beta \varepsilon_M$$

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

Association Contribution

Fraction of hydrogen bond

Yeom, Yoo, Park, Lee (1999)

$$Z_{assoc} = -(N_r / N_A)\nu_{HB}\rho$$

$$\nu_{HB} = \sum_{i=1}^{m}\sum_{j=1}^{n} N_{ij}^{HB} / \sum_{i=1}^{c} N_i r_i$$

$$N_{ij}^{HB} N_r = N_{io}^{HB} N_{oj}^{HB} \exp(-\beta A_{ij}^{HB}) = (N_d^i - \sum_{k=1}^{n} N_{ik}^{HB})(N_a^j - \sum_{k=1}^{m} N_{kj}^{HB}) \exp(-\beta A_{ij}^{HB})$$

Balance equation

Simultaneous nonlinear eqn.

Comparison – pure component parameters

EOS Models	**Parameters**	**T Dependency**	**Procedure To Get Parameters**
*** Non-specific interaction**			
PR-WS	a_i, b_i	a_i **Dependent** b_i **Independent**	**Using critical const. and vapor pressure**
SAFT	$r_i, \varepsilon_i, \sigma_i, e$	**Independent**	**Using vapor pressure and liquid density**
NLF-HB	r_i, ε_{ii}	**Dependent**	**Using vapor pressure and liquid density**
*** Specific interaction (Hydrogen bonding)**			
PR-WS	-	-	-
SAFT	$\varepsilon^{S_iY_j}, \kappa^{S_iY_j}$	**Independent**	**Required for individual species and additional bond formation**
NLF-HB	U^{HB}, S^{HB}	**Independent**	**Depends on the type of hydrogen bond**

Comparison – mixing rule and binary interaction parameters

	PR-WS	*SAFT*	*NLF-HB*
Basis of Mixing Rule	**Based on quadratic composition dependence of B_{ij}**	**Vdw / VF mixing rule** **Results are affected by the choice of mixing rule**	**Do not require empirical mixing rule**
No. of Binary Parameters	**2 (UNIQUAC)** **3 (NRTL)** **k_{ij} calculated**	**1 (k_{ij})**	**1 (k_{ij})**
Procedure	**Fit activity coeff. (obtain k_{ij})**	**Global Optimization of DP and DY**	**Global Optimization of DP and DY**
Cross Association	**0**	**Additional cross association parameters (2)**	**Can be assumed(2)**

Procedures for Wong-Sandler Mixing Rule

☐ Controlled Optimization

- *Using VLE data*
- *Using existing activity model parameters (DDB or UNIFAC, …)*
- *Using infinite dilution activity coefficient*

For given activity coefficient parameters , adjust k_{ij} to match following underlying assumption of Wong-Sandler mixing rule

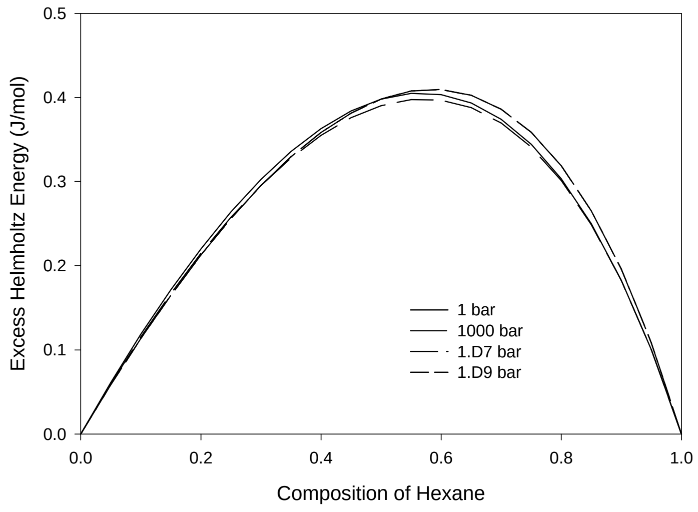
$$G^{ex}(T, P = 1\,\text{bar}, x_i) \approx A^{ex}(T, P = 1\,\text{bar}, x_i) \approx A^{ex}(T, \text{high P}, x_i)$$

☐ Global Optimization

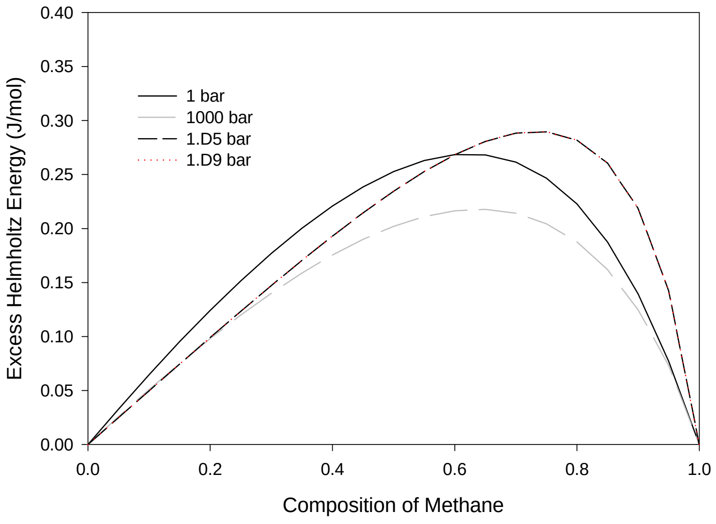
- *Optimization of Gibbs free energy model parameter and k_{ij} value*
- *Can violate the basic assumption*

Sample Calculation – PR-WS can be inconsistent

G^E (at low P) are unavailable for mixtures of light gases at high P



Plot of Excess Helmholtz energy for hexane + hexanol system



Plot of Excess Helmholtz energy for methane + butane system

Controlled optimization

Fit A_{12} and A_{21}

Adjust k_{12} using $A^E=G^E$

Global optimization

Fit A_{12} , A_{21} and k_{12}

Experimental Data for Comparison

	Source	No. of Data
Vapor pressure Liquid denisty	KDB (http::/thermo.korea.ac.kr/kdb)	Total 58 Components
VLE data	Electronic version of DDB	34 systems 82 set 1321 points
Polymer Solubility	Hao et al. (DECHEMA)	4 systems 18 sets 205 points

Vapor Pressure Error

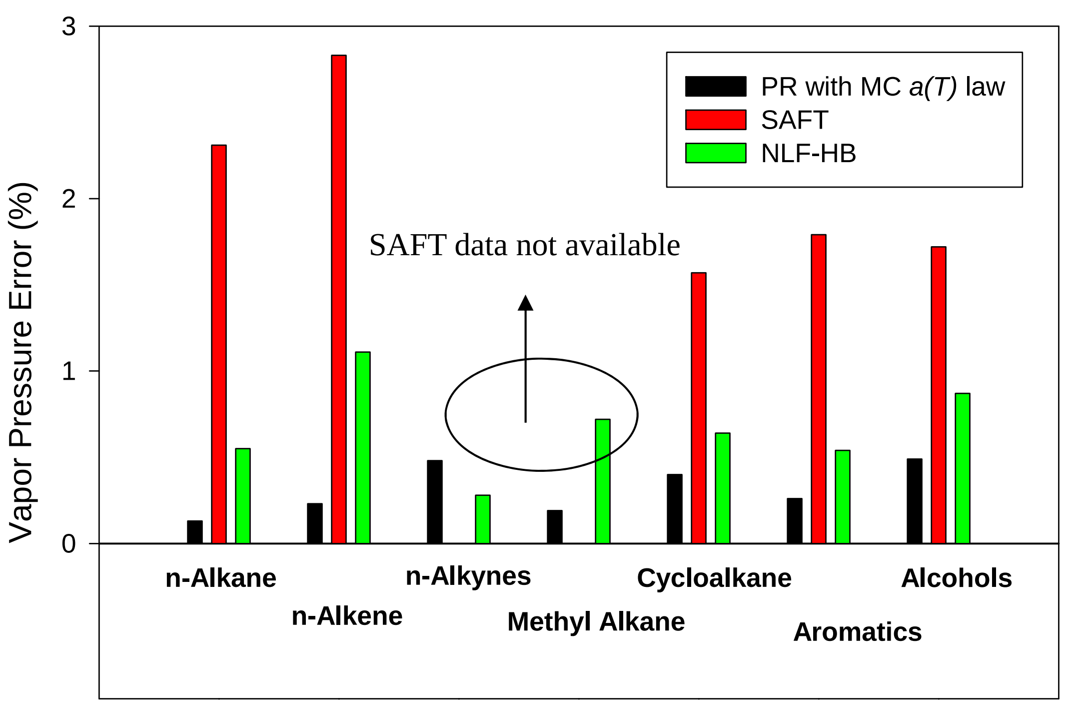


Fig.1 Comparison of vapor pressure error for three EOS models.

$$DP(\%) = \sum_i \sqrt{(P_i^{calc} - P_i^{\exp})^2 / P_i^{\exp 2}}$$

- ***PR-MC is most accurate with 3 T dependent parameters***
- ***SAFT is most inaccurate due to T independent parameters***

	PR-MC	**SAFT**	**NLF-HB**
Average % Error	**0.27**	**2.11**	**0.67**

Liquid Density Error

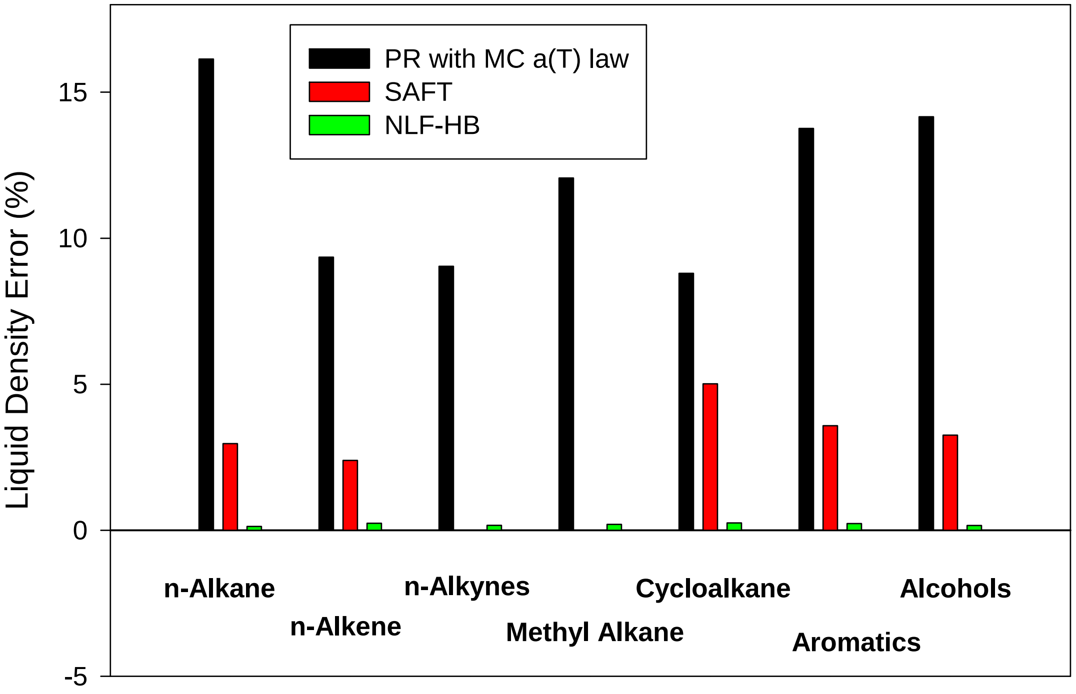


Fig.2 Comparison of saturated liquid density error for three EOS models.

$$D\rho(\%) = \sum_i \sqrt{(\rho_i^{calc} - \rho_i^{\exp})^2 / \rho_i^{\exp^2}}$$

- ***NLF-HB is most accurate with 3 T dependent size parameters***
- ***PR-MC is most inaccurate because liquid density data were not fitted***

	PR-MC	SAFT	NLF-HB
Average % Error	5.27	3.19	0.19

Classification of components and objective function for VLE comparison

- ☐ **NONPOLAR COMPONENTS (NP)**
  - *Non-hydrogen bonding, low dipole moments*
  - *Methane, ethane, …*
- ☐ **ASSOCIATING COMPONENTS (AS)**
  - *Self hydrogen bonding components*
  - *Alcohols, acid, amines, …*
- ☐ **NON-ASSOCIATING COMPONENTS (NA)**
  - *Do not form self-association, weakly polar*
  - *Can form cross-association*
  - *Ketone, ether, ester, aldehyde,…*

$$OBJF = \sum_i \sqrt{(P_i^{calc} - P_i^{\exp})^2 / P_i^{\exp\,2} + (y_i^{calc} - y_i^{\exp})^2 / y_i^{\exp\,2}}$$

$$DP(\%) = \frac{1}{N} \sum_i \left| (P_i^{calc} - P_i^{\exp}) \right| / P_i^{\exp} \times 100$$

$$DY = \sum_i \left| y_i^{calc} - y_i^{\exp} \right| / N$$

System Index : VLE for NP + NP System at low P

- **NP + NP : Hexane + n-Alkane Systems**
  - *C7 : Hexane + Heptane*
  - *C8 : Hexane + Octane*
  - *C10 : Hexane + Decane*
  - *C12 : Hexane + Dodecane*
  - *C16 : Hexane + Hexadecane*

VLE of NP + NP System at low P (hexane + n-alkane)

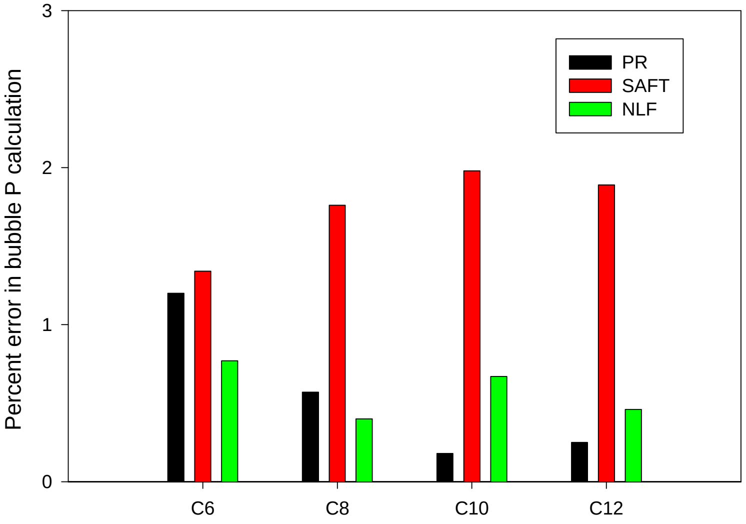


Fig.3 Comparison of error in bubble pressure calculation for NP + NP systems at low P (hexane + n-alkane)

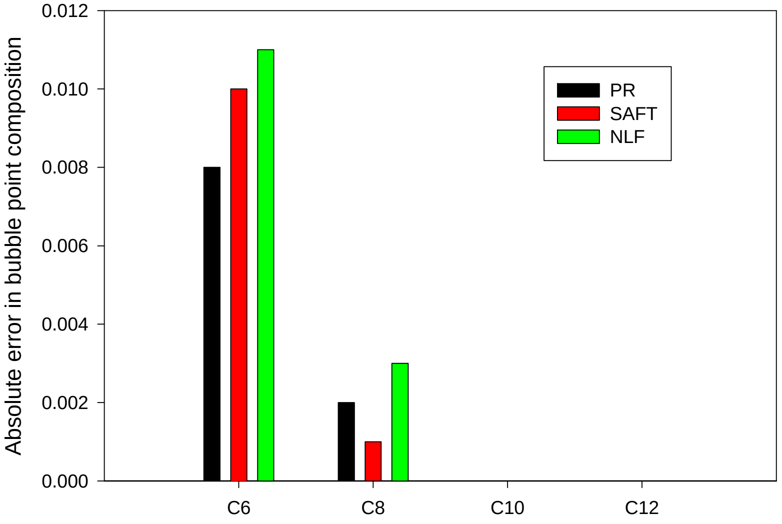


Fig.4 Comparison of error in bubble point compostion calculation for NP + NP systems at low P (hexane + n-alkane)

	PR		SAFT		NLF	
	DP(%)	DY	DP(%)	DY	DP(%)	DY
Average	0.52	0.005	1.69	0.006	0.55	0.007

- *All three EOS model shows good agreements with data (DP < 1-2 %, DY < 0.01)*
- *Although SAFT seems most inaccurate, most error is due to inaccuracy in the pure component vapor pressure*

System Index : VLE for NP + AS System at low P

- ❑ **NP + AS : hexane + 1-alkanol**
  - *OL1 : hexane + methanol*
  - *OL2 : hexane + ethanol*
  - *OL3 : hexane + 1-propanol*
  - *OL4 : hexane + 1-butanol*
  - *OL5 : hexane + 1-pentanol*
  - *OL6 : hexane + 1-hexanol*
  - *OL7 : hexane + 1-heptanol*

VLE of NP + AS System at low P (hexane + 1-alkanol)

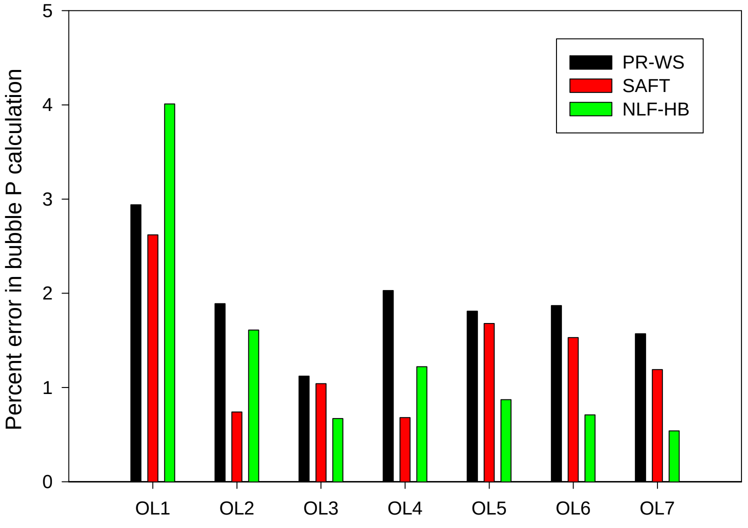


Fig.5 Comparison of error in bubble pressure calculation for NP + AS systems at low P (hexane + 1-alkanol)

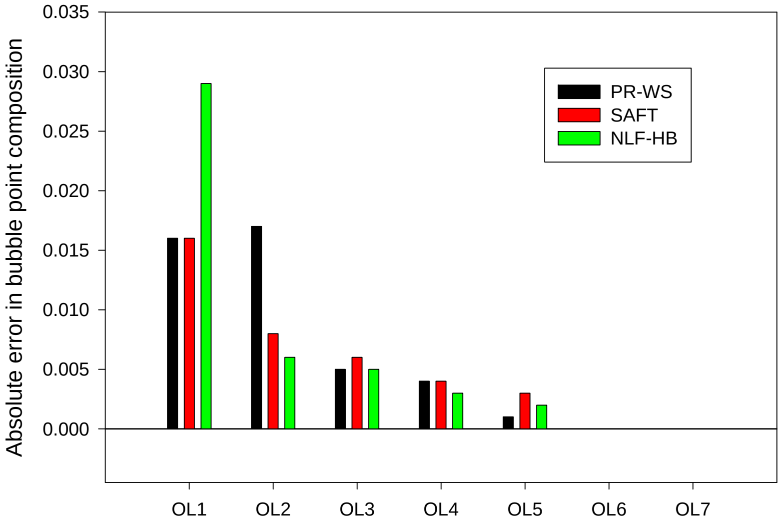


Fig.6 Comparison of error in bubble point compostion calculation for NP + AS systems at low P (hexane + 1-alkanol)

	PR-WS		SAFT		NLF-HB	
	DP(%)	DY	DP(%)	DY	DP(%)	DY
Average	1.89	0.009	1.36	0.008	1.37	0.009

- *All three EOS model shows good agreements with data (DP < 1-2 %, DY < 0.01)*
- *NLF-HB EOS shows better performance as the molecular weight of 1-alkanol becomes larger*

System Index : VLE of NA + NA System at low P

- ❑ **NA + NA : Mixtures of ketone, ether, ester**
  - *DEE293 : acetone + diethyl ether at 293.15 K*
  - *DEE303 : acetone + diethyl ether at 303.15 K*
  - *MA308 : acetone + methyl acetate at 308.15 K*
  - *MA328 : acetone + methyl acetate at 328.15 K*

VLE of NA + NA System at low P (ether,ketone,ester)

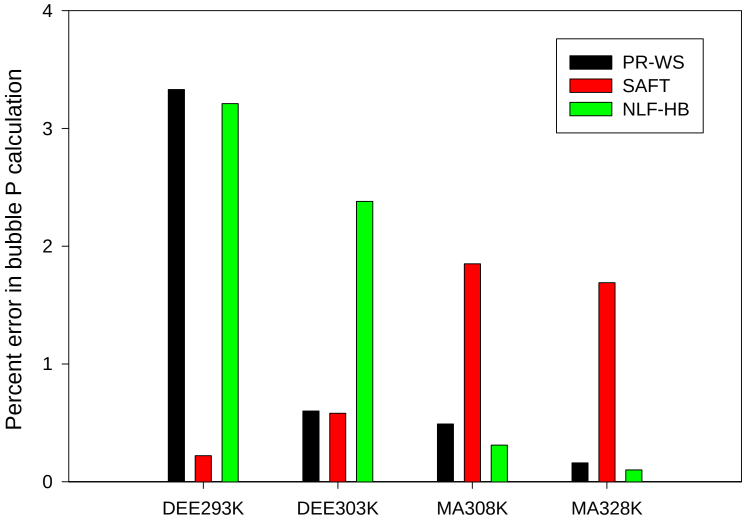


Fig.7 Comparison of error in bubble pressure calculation for NA + NA systems at low P (mixtures with acetone)
< DEE : Diethyl ketone , MA : methyl acetate >

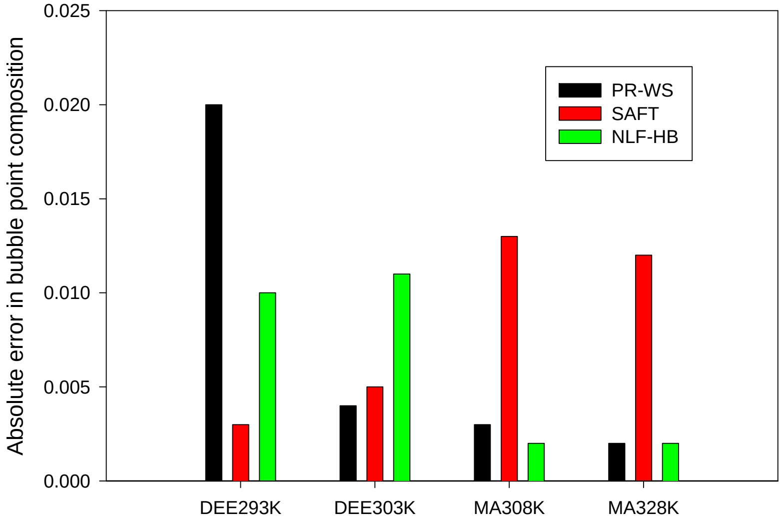


Fig.8 Comparison of error in bubble point compostion calculation for NA + NA systems at low P (mixtures with acetone)
< DEE : Diethyl ketone , MA : methyl acetate >

	PR-WS		**SAFT**		**NLF-HB**	
	DP(%)	**DY**	**DP(%)**	**DY**	**DP(%)**	**DY**
Average	**1.15**	**0.007**	**1.08**	**0.008**	**1.50**	**0.006**

•All three EOS model shows good agreements with data (DP < 1-2 %, DY < 0.01)

•VLE error is mostly determined from pure component property error

(very low vapor pressure)

System Index : VLE of NA + AS System at low P

- ☐ **NA + AS : ketone,ether, ester + 1-alkanol**
  - *1 : acetone + methanol at 298.15 K*
  - *2 : acetone + methanol at 328.15 K*
  - *3 : acetone + ethanol at 305.15 K*
  - *4 : acetone + ethanol at 32815 K*
  - *5 : diethyl ether + methanol at 303.15 K*
  - *6 : diethyl ether + ethanol at 298.15 K*
  - *7 : diethyl ether + ethanol at 313.15 K*
  - *8 : methyl acetate + methanol at 298.15 K*
  - *9 : methyl acetate + methanol at 308.15 K*
  - *10 : methyl acetate + ethanol at 323.15 K*
  - *11 : methyl acetate + ethanol at 333.15 K*

VLE of NA+AS System at low P (1-alcohol + ketone,ether,esters)

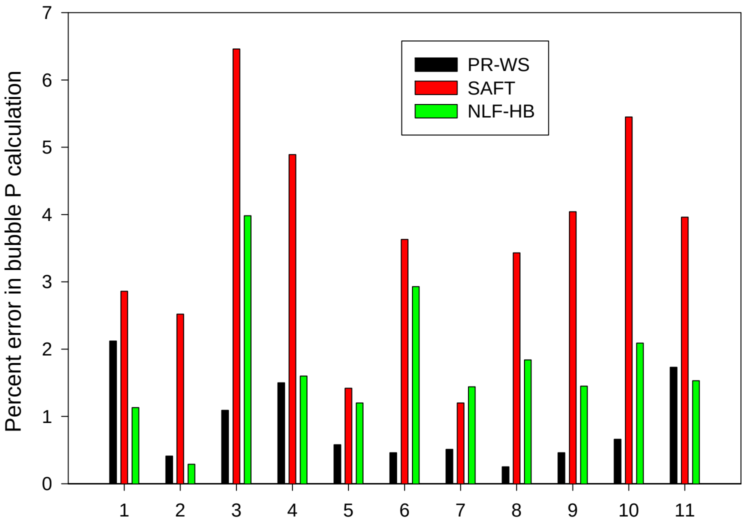


Fig.9 Comparison of error in bubble pressure calculation for AS + NA systems at low P

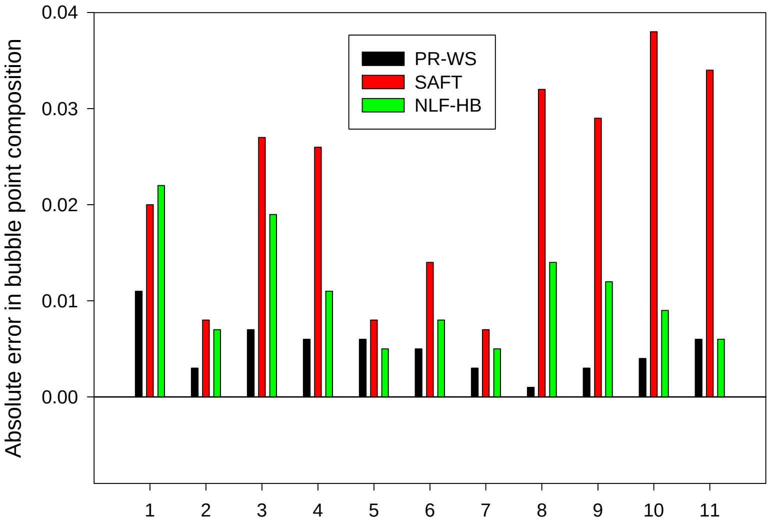


Fig.10 Comparison of error in bubble point compostion calculation for AS + NA systems at low P

	PR-WS		SAFT		NLF-HB	
	DP(%)	DY	DP(%)	DY	DP(%)	DY
Average	0.89	0.005	3.62	0.022	1.77	0.011

- *SAFT and NLF-HB require additional parameters for cross-association*
- *While SAFT seems most inaccurate, the result can be further optimized using more refined cross-association parameters.*
- *NLF-HB shows good performance despite the simplification that cross association energies are the same as those of self association of alcohols*

System index : VLE of AS+AS systems at low P

- ☐ **AS + AS : mixtures of water, alcohol, acid**
  - *A : water + methanol at 298.15 K*
  - *B : water + methanol at 308.15 K*
  - *C : water + methanol at 323.15 K*
  - *D : water + methanol at 373.15 K*
  - *E : water + methanol at 423.15 K*
  - *F : water + ethanol at 298.15 K*
  - *G : water + ethanol at 312.91 K*
  - *H : water + ethanol at 347.94 K*
  - *I : water + ethanol at 413.15 K*
  - *J : water + 1-propanol at 303.15 K*
  - *K : water + 1-propanol at 333.15 K*
  - *L : water + 1-propanol at 352.95 K*
  - *M : water + acetic acid at 293.15 K*
  - *N : water + acetic acid at 298.15 K*
  - *O : water + acetic acid at 303.15 K*

VLE of AS + AS System at low P (mixtures of water,alcohol, acid)

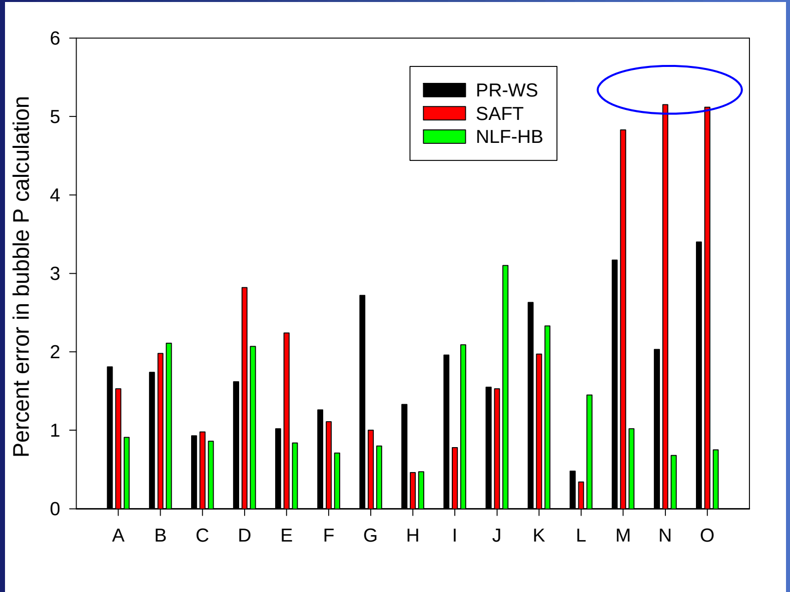


Fig.11 Comparison of error in bubble pressure calculation for AS + AS systems at low P (water, alcohol,acids)

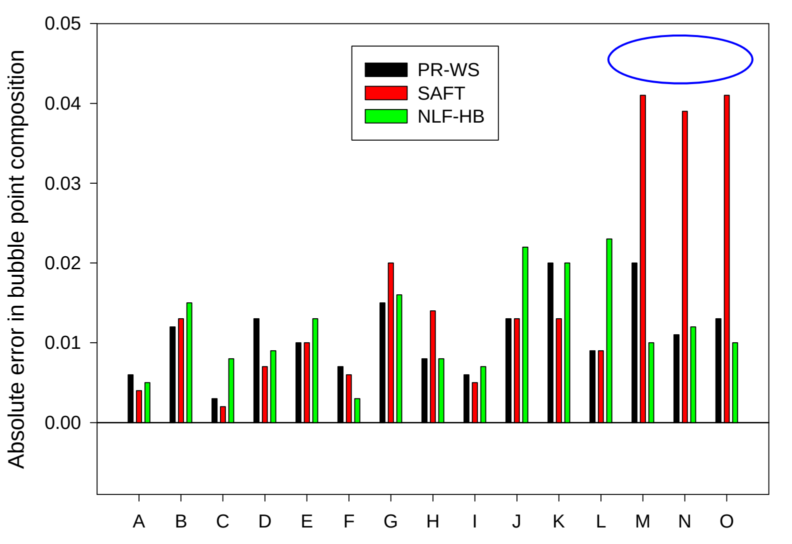


Fig.12 Comparison of error in bubble point compostion calculation for AS + AS systems at low P (water, alcohol,acids)

	PR-WS		**SAFT**		**NLF-HB**	
	DP(%)	**DY**	**DP(%)**	**DY**	**DP(%)**	**DY**
Average	**1.84**	**0.011**	**2.12**	**0.016**	**1.35**	**0.012**

- ***All three EOS model shows good agreements with data (DP < 1-2 %, DY < 0.01)***
- ***NLF-HB shows good result for water + acid systems using the extended hydrogen bonding theory (Park, Kang, Yoo and Lee , 2001)***

Extended hydrogen bonding theory for dimers

- Extended lattice statistics considering dimerization for acids
- Presented at PPEPPD 2001 symposium (poster session)
- New partition function proposed for dimerization

$$g_D = \frac{N_D^1!}{N_{10}^D!(2!)^{N_{11}^H} N_{11}^H!}$$

- Generalized treatment of dimerization and normal association

VLE of water + acetic acid system

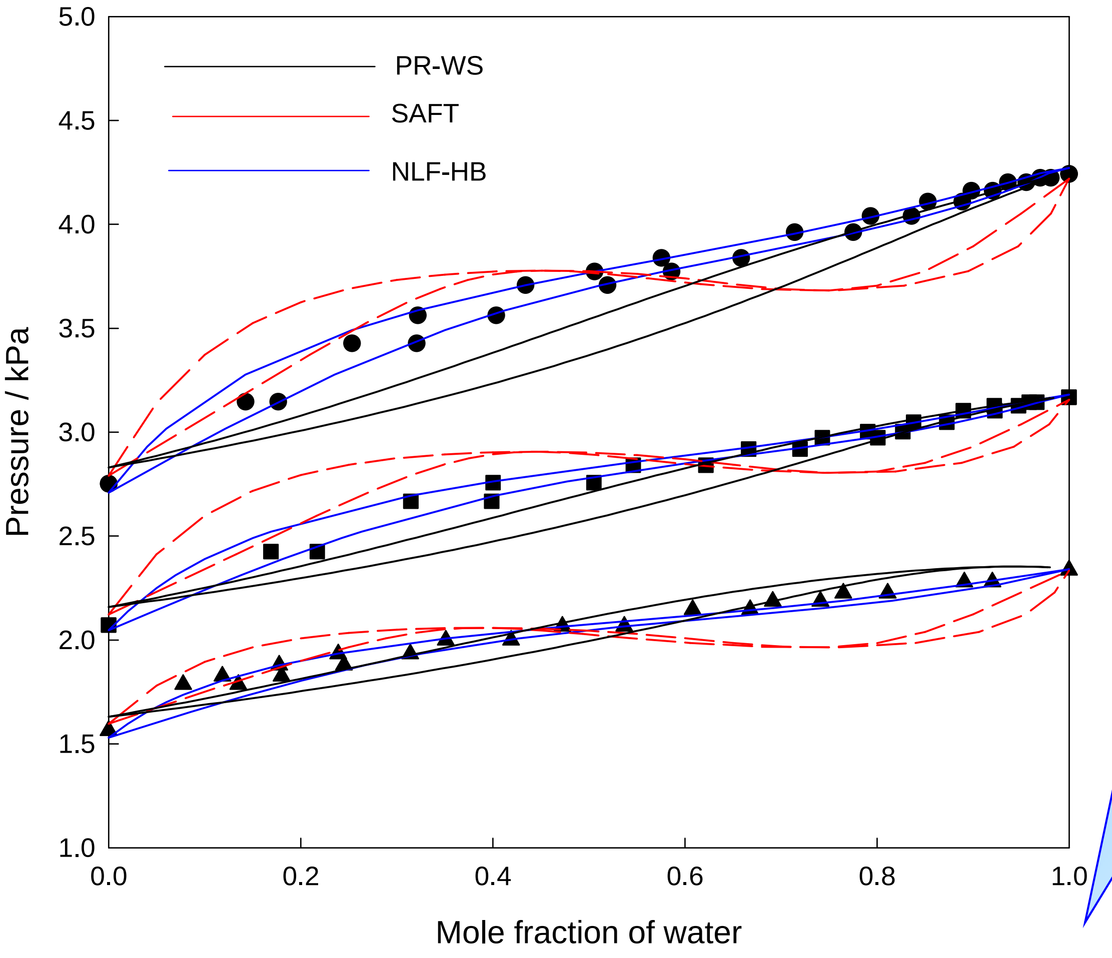


Fig.4 Comparison of Experimental Result with Caculation for Water + Acetic Acid System

•***Very complex behavior of system***

-Self Association (water)

-Dimerization (acid)

-Cross Assocation (acid-water)

• ***NLF-HB shows most accurate result using new extended HB theory***

VLE of NP + NP systems at high P

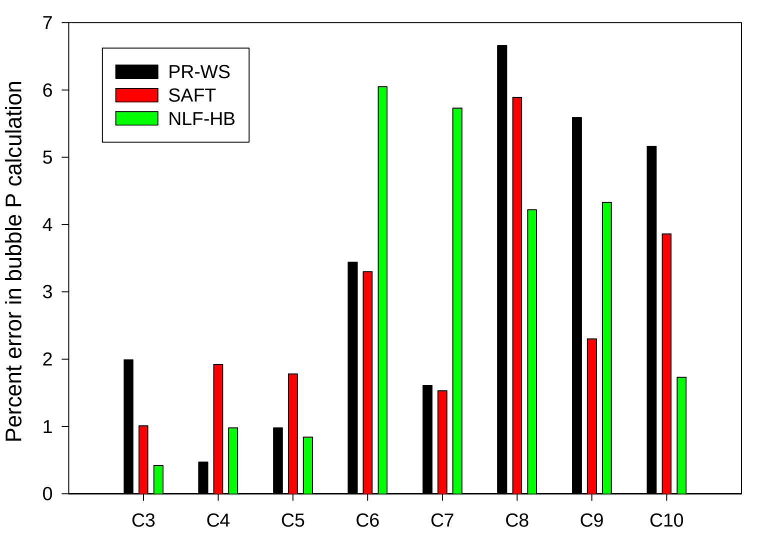


Fig.13 Comparison of error in bubble pressure calculation for NP + NP systems at high P (methane + n-alkane)

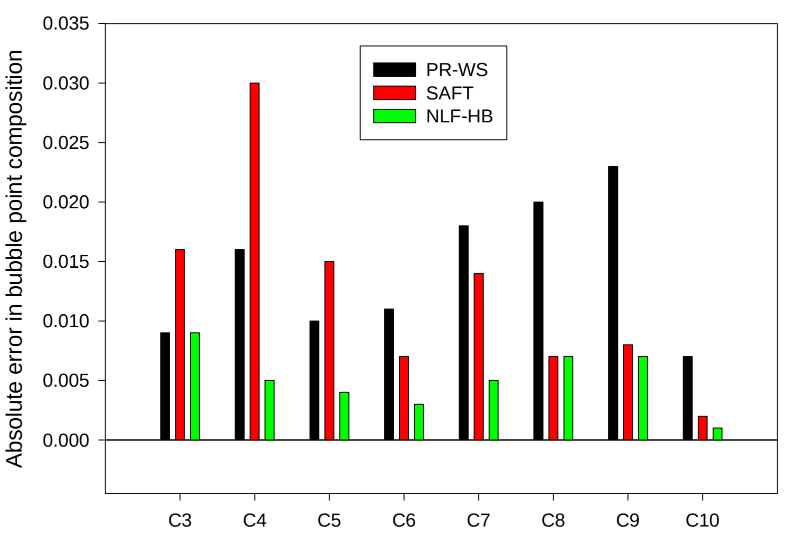


Fig.14 Comparison of error in bubble point compostion calculation for NP + NP systems at high P (methane + n-alkane)

	PR-WS		**SAFT**		**NLF-HB**	
	DP(%)	**DY**	**DP(%)**	**DY**	**DP(%)**	**DY**
Average	**3.24**	**0.014**	**2.70**	**0.012**	**3.04**	**0.005**

- ***All the results were greatly influenced by the pure component parameters outside the normal range (supercritical condition)***
- ***SAFT shows good result using the more parameter for light molecules (e)***

NP + AS systems at high P (CO_2 + alcohol)

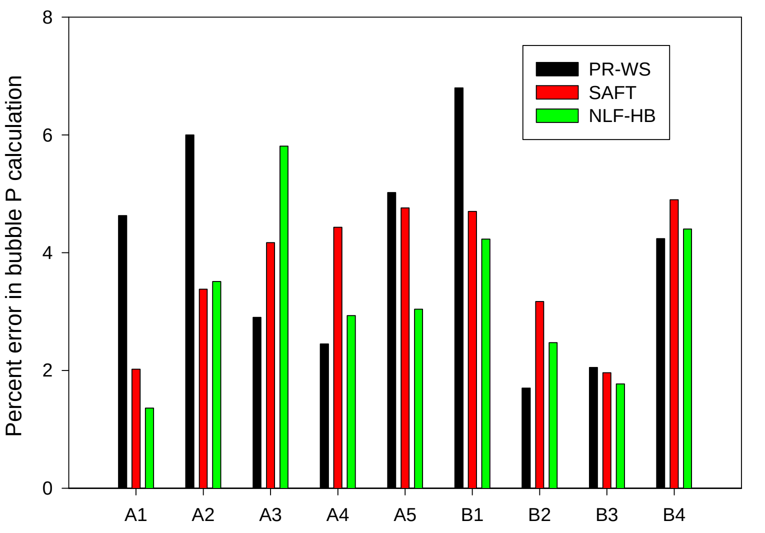


Fig.15 Comparison of error in bubble pressure calculation for NP + AS systems at high P (carbon dioxide + alcohol) < A: CO2 + methanol / B : CO2 + ethanol >

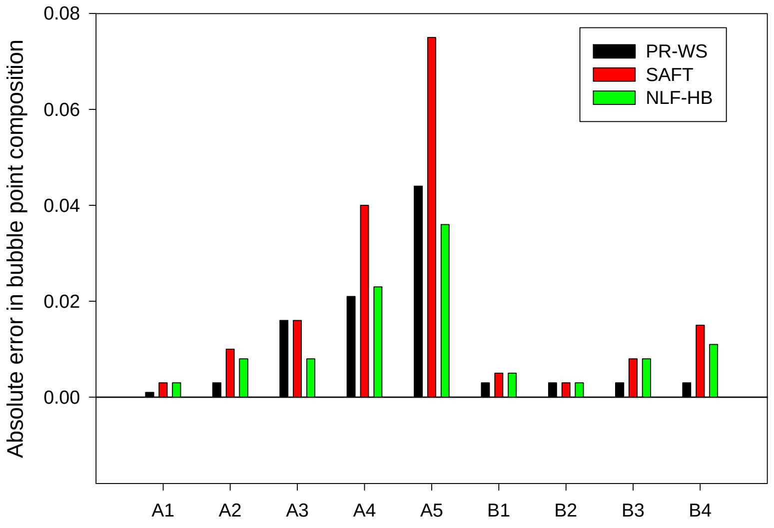


Fig.16 Comparison of error in bubble point compostion calculation for NP + AS systems at high P (carbon dioxide + alcohol) < A: CO2 + methanol / B : CO2 + ethanol >

	PR-WS		**SAFT**		**NLF-HB**	
	DP(%)	**DY**	**DP(%)**	**DY**	**DP(%)**	**DY**
Average	**3.98**	**0.011**	**3.72**	**0.019**	**3.28**	**0.012**

- ***Similar trend as the previous slideCalculation failed for PR-WS***
- ***SAFT and NLF-HB shows inaccurate result***

Polymer Solubility for NP + NP mixtures

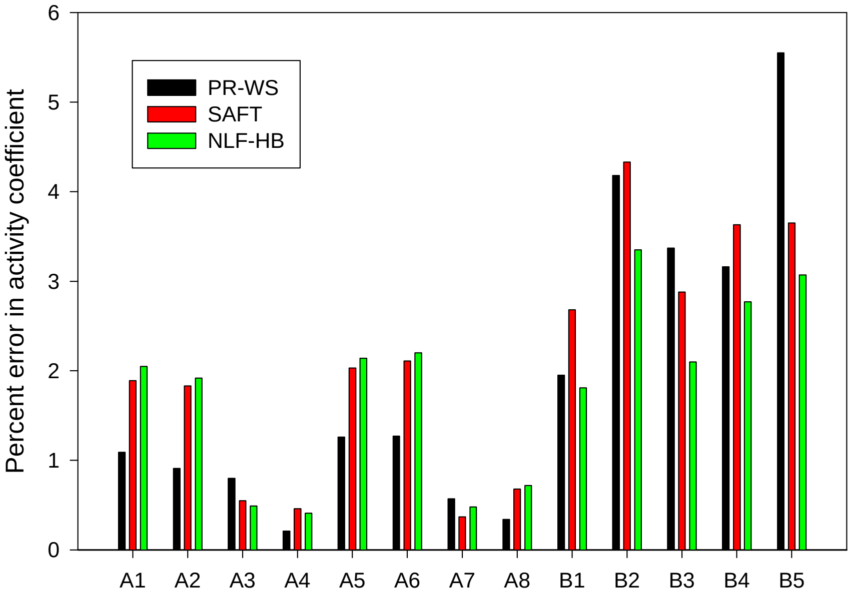


Fig.17 Comparison of activity calculation result for NP (solvent) + NP (polymer) systems
< A : benzene + PS / B: benzene + PIB >

- ***All three EOS model shows good agreement with data***

	PR-WS	**SAFT**	**NLF-HB**
Average % Error	**1.90**	**2.08**	**1.81**

Polymer solubility for AS + NA mixtures

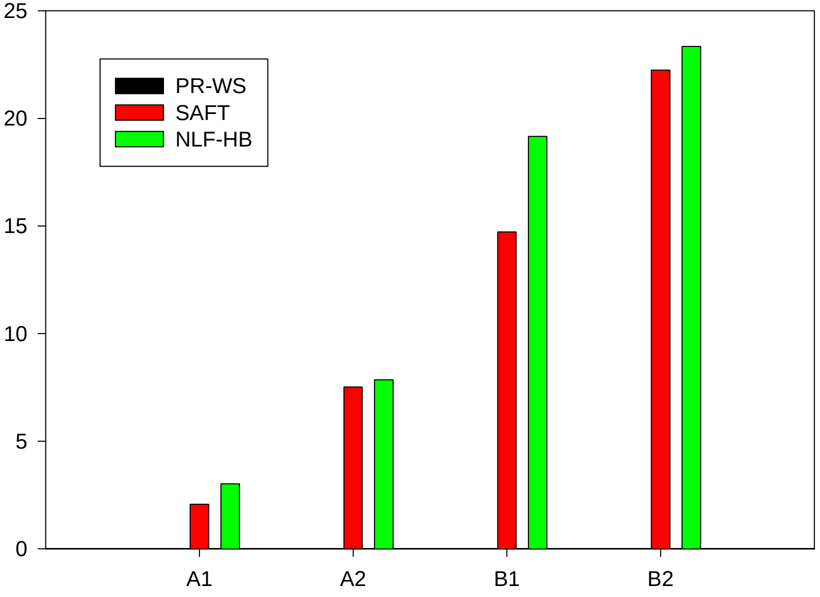


Fig.17 Comparison of activity calculation result for
NP + NA systems
< A : benzene + PVA / B: DEK + PP>

- ***Calculation failed for PR-WS***
- ***SAFT and NLF-HB shows inaccurate result***

	PR-MC	SAFT	NLF-HB
Average % Error	**-**	**13.6**	**15.8**

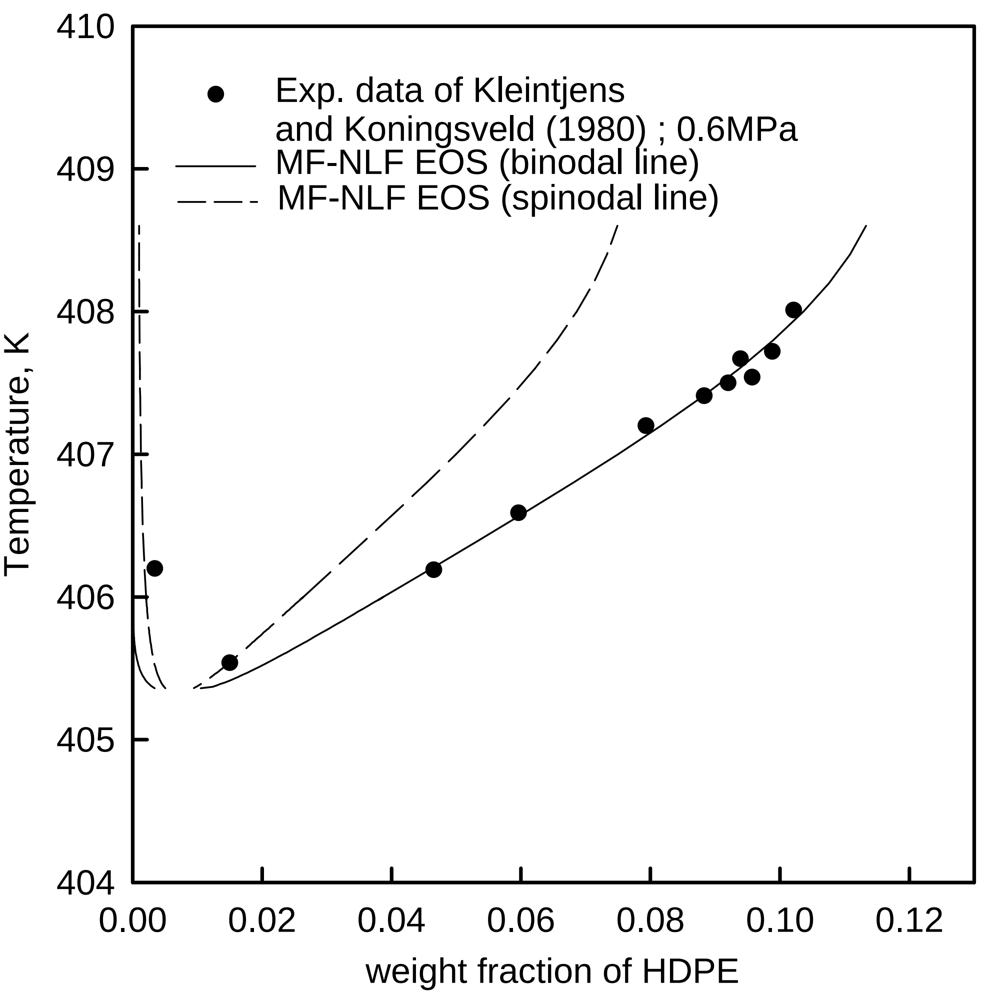
Polymer solubility calculations using PR-WS EOS

❑ **Result of Orbey and Sandler (AIChE J. 1994)**

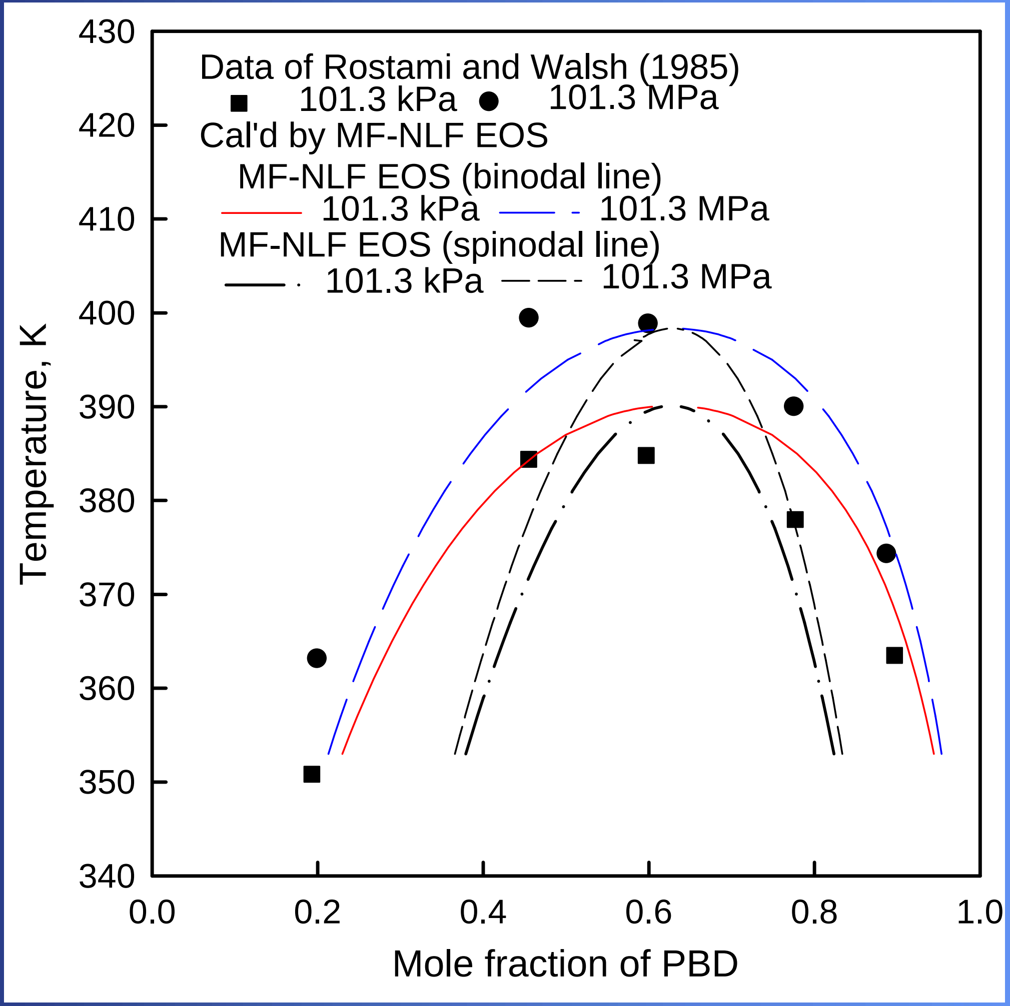
- *k_{ij} value range : 0.77 to 0.97 for* NP + NP *systems*

❑ **k_{ij} value failed to match underlying assumption within meaningful range (-1 to 1) of binary parameters for NP + AS polymer solubility**

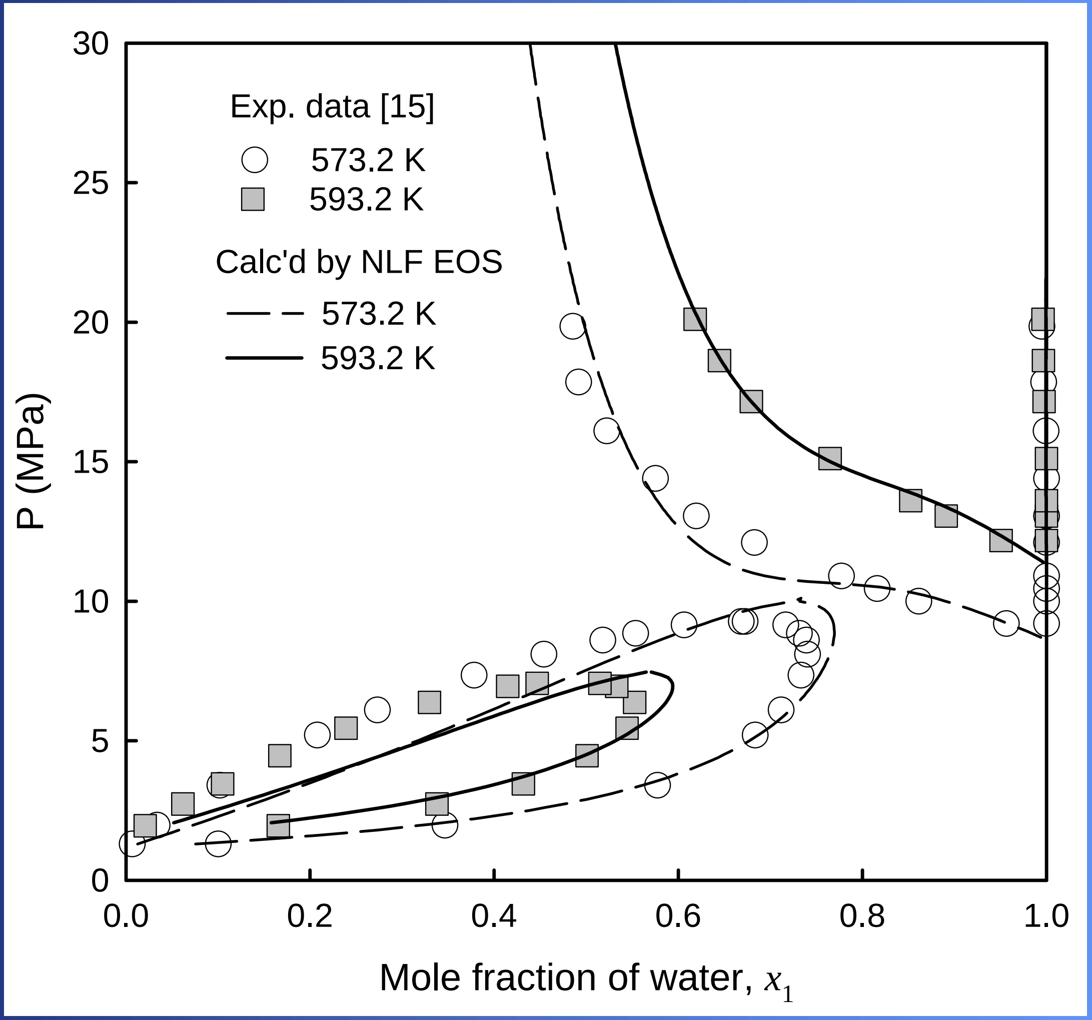
Complex phase behavior - LLE calculation for HDPE + hexane



Complex phase behavior – LLE of PB + PS blends



Phase behavior of water + decane system



Computational Aspects

	PVT Behavior	Computation speed	Remark
PR-WS	Simple	Fast	Can violate basic assumption using some parameter sets.
SAFT	Complex	Slow (10 times NLF-HB)	Extra computation time for balance eqn. solving when two or more types of association
NLF-HB	Relatively simple	Relatively fast (4 time PR-WS)	Extra computation time for balance eqn. solving when two or more types of association

Sensitivity of Binary Interaction Parameters

$$\frac{dP}{dk_{ij}} = \frac{P(1.01k_{ij}) - P(0.99k_{ij})}{0.02k_{ij}}$$

$$\frac{dY}{dk_{ij}} = \frac{y_1(1.01k_{ij}) - y_1(0.99k_{ij})}{0.02k_{ij}}$$

- ***All the EOS model have small derivatives with respect to paramters -> robust behavior of binary interaction parameters***

System	EOS	Temperature	dP/dKij	dY/dKij
Hexane + Hexadecane	PR-WS	293.15	**0.04**	**0.00003**
	NLF-HB	293.15	0.62	0.00152
	SAFT	293.15	0.57	0.00092
Hexane + 1-Hexanol	PR-WS	293.15	**0.30**	**0.02600**
	NLF-HB	293.15	0.69	0.08100
	SAFT	293.15	0.69	0.00699
Methanol + Water	PR-WS	298.15	0.22	1.52000
	NLF-HB	298.15	**0.15**	**1.09000**
	SAFT	298.15	0.26	1.91000

Error increase due to T difference in VLE sets

- *System : n-Hexane + 1- Propanol*

T (deg.C)	K_{ij}	PR-WS		SAFT		NLF-HB	
		DP	DY	DP	DY	DP	DY
25	Optimum	1.82	0.0044	1.33	0.002	1.14	0.003
75	Optimum	2.97	0.0177	1.74	0.010	2.92	0.012
75	Value at 25 deg.C	3.27	0.0151	3.85	0.023	2.99	0.019
Increase in error		0.30	-0.0026	2.11	0.013	0.07	0.007

- *All three EOS models do not significantly affected by the temperature dependency of parameters*
- *Among 3 EOS models, SAFT EOS is most sensitive for this specific system*

Conclusion

- Pure Properties (58 comp.s) and VLE (82 isotherms) were compared for PR-WS, SAFT and NLF-HB EOS.
- For pure components, NLF-HB gives best result due to temperature dependent pure component parameters.
- For VLE calculation most EOS considered showed similar degree of prediction.
- For AS + AS systems, new extended HB model shows better result than the other two EOS models
- For computational aspect, PR-WS EOS is fast and easy, while SAFT is most complex and time-consuming.
- All three EOS model showed robust result with respect to change in interaction parameters

Kyong Hoe Ru - Pavillion

Faces of Ancient Korean

Korea-Japan 2002 World Cup
(who will be the winner ?)

Ancient statue
Bodhisattva
(A.D. 6 to 7)