Excess enthalpy and Vapor-Liquid Equilibrium prediction using NLF and NLF-HB Theory

Kwon, Jung Hun

Thermodynamics and Properties Lab.

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I. Nonrandom Lattice Fluid Theory (**NLF Theory**)

II. Hydrogen Bonding Nonrandom Lattice Fluid Theory (**NLF-HB Theory**)

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Development

Sanchez and Lacombe (1976)

Okada and Nose (1981)

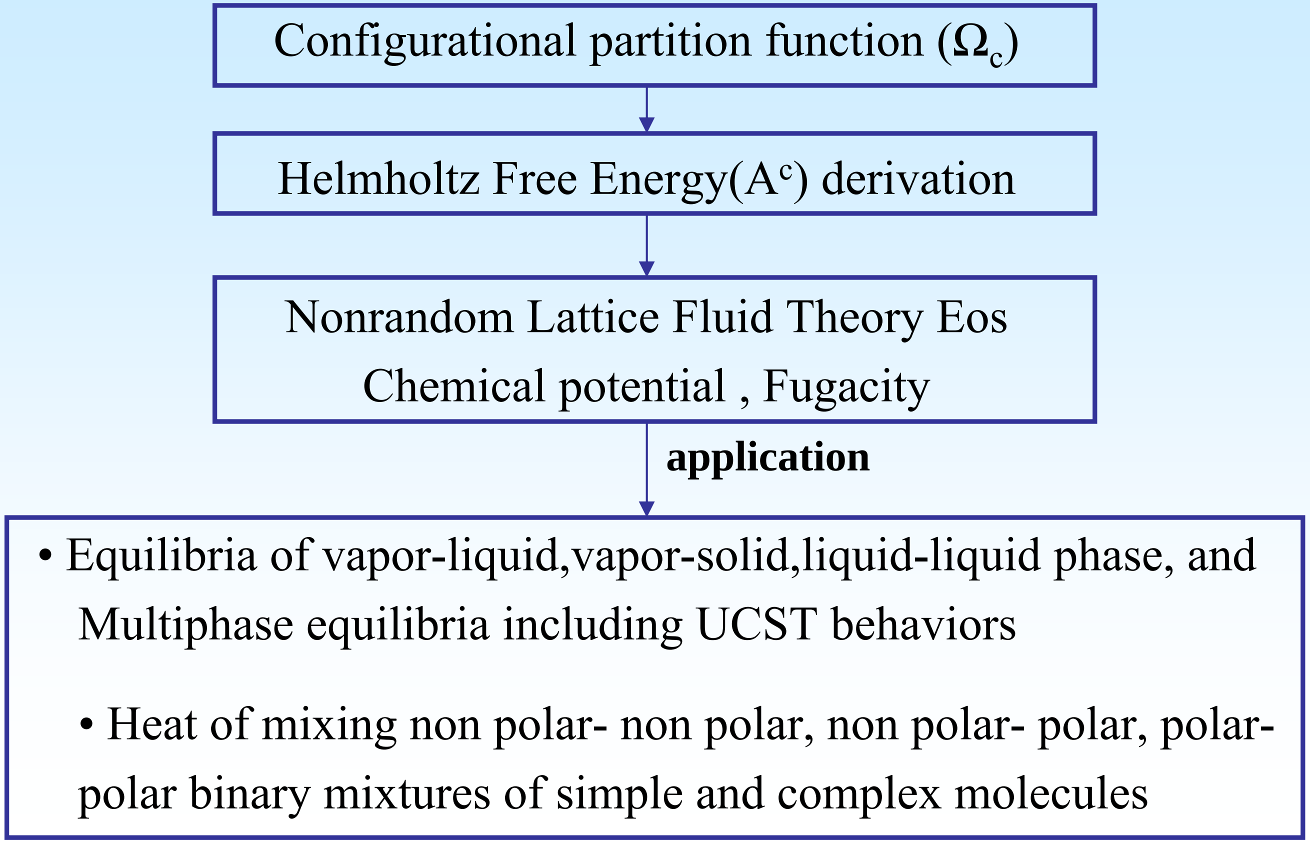
Panayiotou and Vera (1982)

Kumar (1986)

You et al. (NLF) (1994)

I. NLF Theory (1)

- Assumption : consideration of hole' non-randomness



Configurational partition function (Ω_c)

Helmholtz Free Energy(A^c) derivation

Nonrandom Lattice Fluid Theory Eos
Chemical potential , Fugacity

application

- Equilibria of vapor-liquid,vapor-solid,liquid-liquid phase, and Multiphase equilibria including UCST behaviors
- Heat of mixing non polar- non polar, non polar- polar, polar-polar binary mixtures of simple and complex molecules

I. NLF Theory (2)

Helmholtz Free Energy
(A) $\xrightarrow{\text{expansion}}$ Expression for
Thermodynamic properties

1. Partition Function

(1) Nonrandom Lattice Fluid Model Term

In a three-dimension lattice,

- ► The coordination number : z =10
- ► Unit cell volume : V_H = 9.75 cm^3/mol
- ► Effective surface area : $zq_i = (z_i - 2)r_i + 2$

(2) Configurational partition function (Ω_c)

- $\Omega c = g_R g_{NR} \exp(-\beta U^c)$

$$\Omega c = \left[\frac{N_r!}{\Pi N_i!}\right]\left[\frac{N_q!}{N_r!}\right]^{z/2}\left[\frac{\Pi N^o{}_{ii}\Pi\left[\left(\frac{N^o{}_{ij}}{2}\right)!\right]^2}{\Pi N_{ii}!\Pi\left[\left(\frac{N_{ij}}{2}\right)!\right]^2}\right]\exp(-\beta U^C)$$

(3) Connection of thermodynamic function with configurational function

- $\beta A^c = -\ln \Omega^c$

$$A^C = A^{C0} + \sum\sum_{i\geq j}\left(\frac{\partial A^c}{\partial \varepsilon_{ij}}\right)^0 \varepsilon_{ij} + \left(\frac{1}{2}\right)\sum\sum_{i\geq j}\sum\sum_{k\geq l}\left(\frac{\partial^2 A}{\partial \varepsilon_{kl}\partial \varepsilon_{ij}}\right)\varepsilon_{ij}\varepsilon_{kl} + \cdots\cdots\cdots$$

(4) $$\beta A^C = N_0 \ln N_0 - N_0 + N_1 \ln N_1 + N_2 \ln N_2 + \ldots$$

$$- N_r \ln N_r + N_r - (\frac{z}{2})[N_q \ln N_q - N_q - N_r \ln N_r + N_r]$$

$$-\left(\frac{z\beta N_q}{2}\right)\left[\sum\sum \theta_i\theta_j\varepsilon_{ij} + \left(\frac{\beta}{2}\right)\sum\sum\sum\sum \theta_i\theta_j\theta_k\theta_l\varepsilon_{ij}(\varepsilon_{ij} + \varepsilon_{kl} - \varepsilon_{ik} - \varepsilon_{jk})\right] + \ldots$$

2. Expression of Thermodynamic properties

(1) $$P = -\left(\frac{\partial A^C}{\partial V}\right)_{T,N_i} = -\frac{1}{v_H}\left(\frac{\partial A^C}{\partial N_0}\right)_{T,N_i} = -\frac{1}{v_H \beta}\left(\frac{\partial \beta A^C}{\partial N_0}\right)_{T,N_i}$$

(2) [illegible]

(3) $$H^E = (U^C + PV)_{mixture} - \sum x_i (U^C + PV)_{pure,i}$$

The molar configurational internal energy for mixture

- $$\frac{\beta U^c}{N} = -\left(\frac{T}{N}\right)\left(\frac{\partial \beta A^c}{\partial T}\right)_{N_0, N_i}$$

$$= \frac{zq_M'}{2} \ln\left[1 + \left(\frac{q_M}{r_M} - 1\right)\rho\right]$$

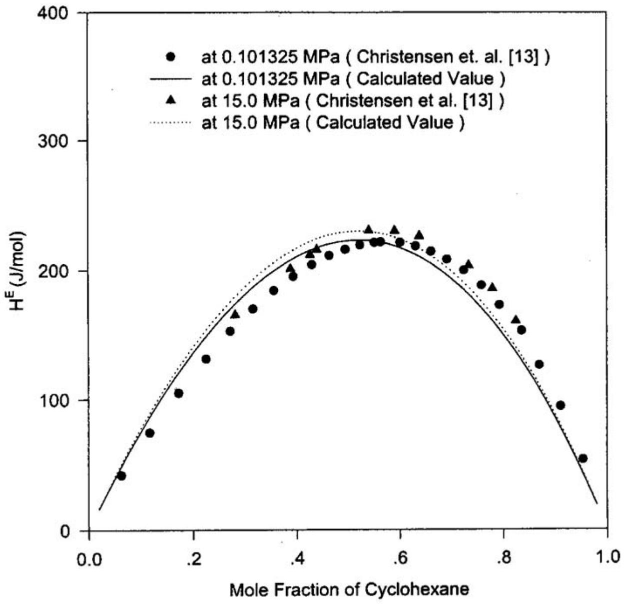
$$+ \frac{z\beta q_M}{2\theta}\left[\sum\sum \theta_i \theta_j \varepsilon_{ij}\left(\frac{q_i'}{q_i} + \frac{q_j'}{q_j} - \frac{q_M'}{q_M}\theta + \frac{\varepsilon_{ij}'}{\varepsilon_{ij}} - 1\right) + \frac{\beta}{2}\sum\sum\sum\sum \theta_i \theta_j \theta_k \theta_l \varepsilon_{ij}\right.$$

$$\times \left\{(\varepsilon_{ij} + \varepsilon_{kl} - \varepsilon_{ik} - \varepsilon_{jk})\left(\frac{q_i'}{q_i} + \frac{q_j'}{q_j} + \frac{q_M'}{q_M}\theta + \frac{\varepsilon_{ij}'}{\varepsilon_{ij}} - 2\right)\right.$$

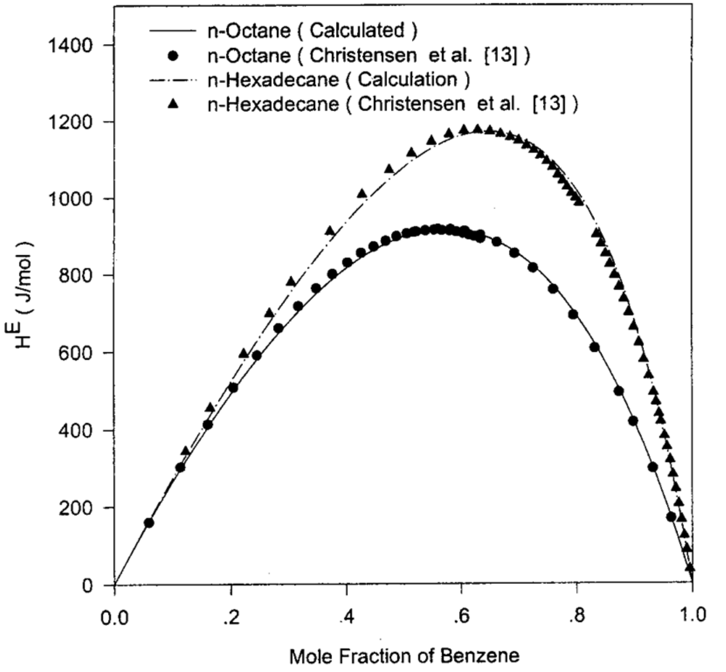
$$- \frac{q_M'}{q_M}\theta(2\varepsilon_{ij} + 4\varepsilon_{kl} - 3\varepsilon_{ik} - 3\varepsilon_{jk}) + \varepsilon_{ij}' + \varepsilon_{kl}' - \varepsilon_{ik}' - \varepsilon_{jk}'$$

$$\left.\left. + \frac{q_k'}{q_k}(\varepsilon_{kl} - \varepsilon_{ik} - \varepsilon_{jk}) + \frac{q_l'}{q_l}\varepsilon_{kl}\right\}\right]$$

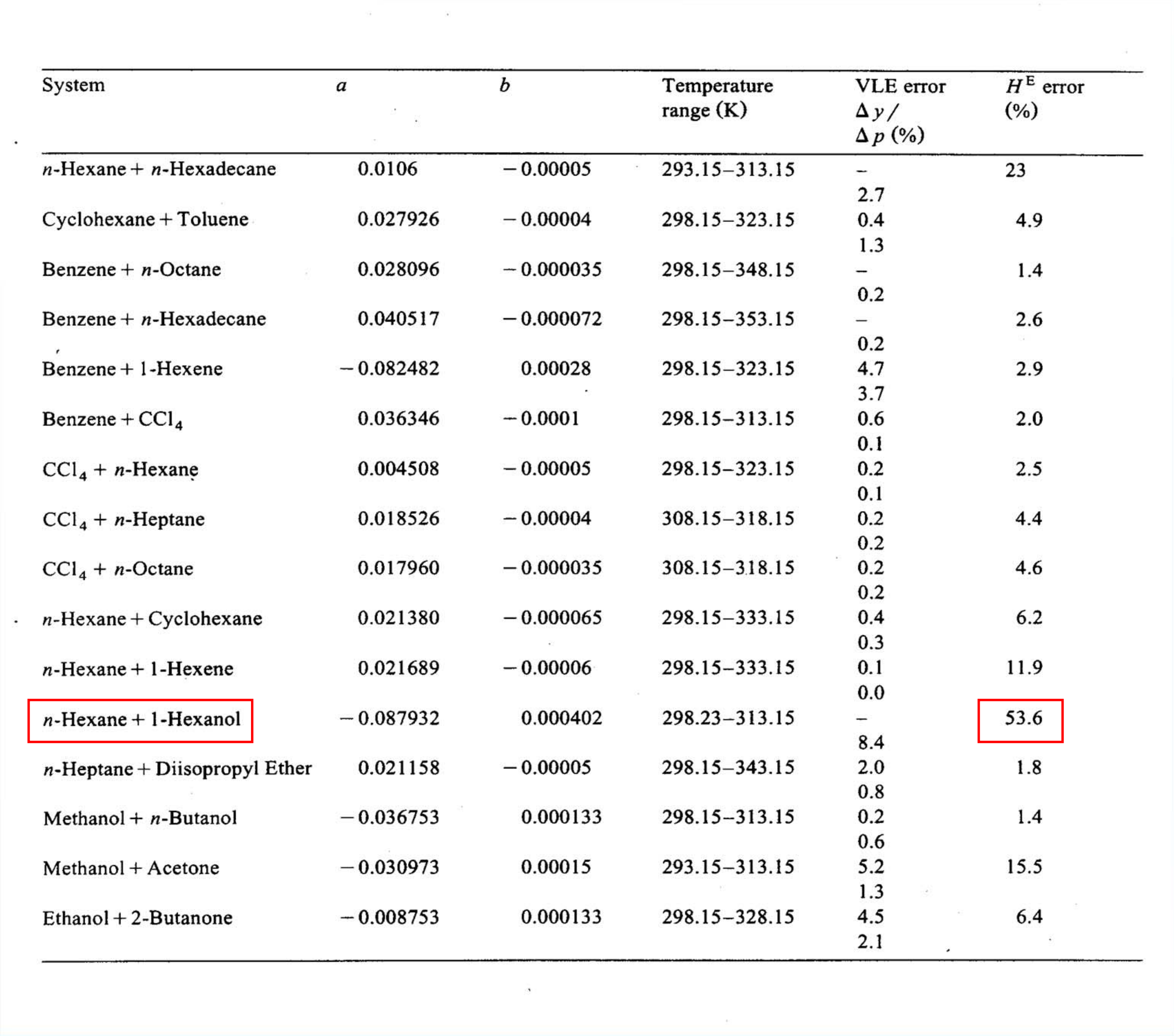
Comparison of calculated excess enthalpies for binary system



Comparison of calculated excess enthalpies for *cyclohexane* + *n-hexane* system with Experimental results at 298K and different pressures (0.10315 and 15.0 Mpa).



Comparison of calculated excess enthalpies for *benzene* + *n-alkane* system with Experimental results at 298K and 0.10315 Mpa.



System	a	b	Temperature range (K)	VLE error Δy / Δp (%)	H^E error (%)
n-Hexane + n-Hexadecane	0.0106	−0.00005	293.15–313.15	– 2.7	23
Cyclohexane + Toluene	0.027926	−0.00004	298.15–323.15	0.4 1.3	4.9
Benzene + n-Octane	0.028096	−0.000035	298.15–348.15	– 0.2	1.4
Benzene + n-Hexadecane	0.040517	−0.000072	298.15–353.15	– 0.2	2.6
Benzene + 1-Hexene	−0.082482	0.00028	298.15–323.15	4.7 3.7	2.9
Benzene + CCl_4	0.036346	−0.0001	298.15–313.15	0.6 0.1	2.0
CCl_4 + n-Hexane	0.004508	−0.00005	298.15–323.15	0.2 0.1	2.5
CCl_4 + n-Heptane	0.018526	−0.00004	308.15–318.15	0.2 0.2	4.4
CCl_4 + n-Octane	0.017960	−0.000035	308.15–318.15	0.2 0.2	4.6
n-Hexane + Cyclohexane	0.021380	−0.000065	298.15–333.15	0.4 0.3	6.2
n-Hexane + 1-Hexene	0.021689	−0.00006	298.15–333.15	0.1 0.0	11.9
n-Hexane + 1-Hexanol	−0.087932	0.000402	298.23–313.15	– 8.4	53.6
n-Heptane + Diisopropyl Ether	0.021158	−0.00005	298.15–343.15	2.0 0.8	1.8
Methanol + n-Butanol	−0.036753	0.000133	298.15–313.15	0.2 0.6	1.4
Methanol + Acetone	−0.030973	0.00015	293.15–313.15	5.2 1.3	15.5
Ethanol + 2-Butanone	−0.008753	0.000133	298.15–328.15	4.5 2.1	6.4

List of binary parameters and comparison of results with experimental data

II. NLF-HB Theory (1)

[Veytsman Statistics]

- ▣ Donors and acceptors distribution

$$\prod_i \frac{N_d^i!}{N_{i0}!} \prod_j \frac{N_a^i!}{N_{0j}!} \prod_i \prod_j \frac{1}{N_{ij}!}$$

- ▣ Probability of Hydrogen Bonding

$$P_{ij} = z l_{ij} / N$$

- ▣ The Veytsman statistics

$$\prod_i \frac{N_d^i!}{N_{i0}!} \prod_j \frac{N_a^i!}{N_{0j}!} \prod_i \prod_j \frac{1}{N_{ij}!} \frac{1}{N_r^{N_{HB}}} \exp(-\sum_i \sum_j \beta N_{ij} A_{ij})$$

II. NLF-HB Theory (2)

▶ Configurational partition function (Ω_c)

$$\Omega \quad = \Omega_{PHYS} \, \Omega_{HB}$$

- Ω_{PHYS} : [Physical term]… You et al. (1994)
- Ω_{HB} : [Chemical term] … Extension of Veytsman statistics

▣ The total number of donor groups of type *k* : $N^k{}_d = \sum_i d^i{}_k N_i$

▣ The total number of acceptor groups of type *l* : $N^l{}_a = \sum_i a^i{}_l N_i$

- $d^i{}_k$: The number of *k*-type of proton donor for molecule *i*
- $a^i{}_l$: The number of *l*-type of proton acceptor for molecule *i*

- The total number of hydrogen-bonded pair

$$N^{HB}=\sum_{k}^{K}\sum_{l}^{L}N^{HB}{}_{kl}$$

- The number of proton donors and acceptors that do not participate in the hydrogen bonding pairs

$$N_{k0}=N^{k}{}_{d}-\sum_{l}N^{HB}{}_{kl}$$

$$N_{l0}=N^{l}{}_{a}-\sum_{k}N^{HB}{}_{kl}$$

- Partition Function of the Veytman statistics

$$\Omega^{c}{}_{HB}=\frac{1}{N_{r}{}^{N^{HB}}}\prod_{k}^{K}\frac{N^{k}{}_{d}!}{N_{k0}!}\prod_{l}^{L}\frac{N^{l}{}_{a}!}{N_{l0}!}\prod_{k}^{K}\prod_{l}^{L}\frac{1}{N_{kl}{}^{HB}!}\exp(-\beta N_{kl}{}^{HB}A_{kl})$$

▣ The complete statistical formulation for the hydrogen bonding

$$\Omega_{HB} = \prod_{k=1}^{M} \frac{N_{k0}^{H0}!}{N_{k0}^{H}!} \prod_{j=1}^{N} \frac{N_{0l}^{H0}!}{N_{0l}^{H}!} \prod_{k=1}^{M} \prod_{l=1}^{N} \frac{N_{kl}^{H0}!}{N_{kl}^{H}!} (P_{kl})^{(N_{kl}^{H} - N_{kl}^{H0})} \exp(-\beta A_{kl}^{H} N_{kl}^{H})$$

$$P_{kl} = r_H / N_r$$

P_{kl} : Probability of finding an acceptor site around donor site

▣ Expression of excess enthalpy

$$H^{E} = (U^{C} + PV)_{mixture} - \sum x_i (U^{C} + PV)_{pure,i}$$

The molar configurational internal energy for mixture
(NLF-HB)

- $$\frac{\beta U^c}{N} = -\left(\frac{T}{N}\right)\left(\frac{\partial \beta A^c}{\partial T}\right)_{N_0, N_i}$$

$$= \frac{z q_M'}{2} \ln\left[1 + \left(\frac{q_M}{r_M} - 1\right)\rho\right]$$

$$+ \frac{z\beta q_M}{2\theta}\left[\sum\sum \theta_i \theta_j \varepsilon_{ij}\left(\frac{q_i'}{q_i} + \frac{q_j'}{q_j} - \frac{q_M'}{q_M}\theta + \frac{\varepsilon_{ij}'}{\varepsilon_{ij}} - 1\right) + \frac{\beta}{2}\sum\sum\sum\sum \theta_i \theta_j \theta_k \theta_l \varepsilon_{ij}\right.$$

$$\times \left\{\left(\varepsilon_{ij} + \varepsilon_{kl} - \varepsilon_{ik} - \varepsilon_{jk}\right)\left(\frac{q_i'}{q_i} + \frac{q_j'}{q_j} + \frac{q_M'}{q_M}\theta + \frac{\varepsilon_{ij}'}{\varepsilon_{ij}} - 2\right)\right.$$

$$- \frac{q_M'}{q_M}\theta\left(2\varepsilon_{ij} + 4\varepsilon_{kl} - 3\varepsilon_{ik} - 3\varepsilon_{jk}\right) + \varepsilon_{ij}' + \varepsilon_{kl}' - \varepsilon_{ik}' - \varepsilon_{jk}'$$

$$\left.\left. + \frac{q_k'}{q_k}\left(\varepsilon_{kl} - \varepsilon_{ik} - \varepsilon_{jk}\right) + \frac{q_l'}{q_l}\varepsilon_{kl}\right\}\right] - \frac{z}{z-2} q_M' \nu_{HB} \rho - \sum_i \sum_j \left(\frac{U_{ij}}{kT}\right) \nu_{ij} r_M$$

[Physical Parameters]

① Coordination number : $z = 10$

② Lattice volume : $V_H = 9.75\ cm^3/mol$

③ Pure parameters (r_i, ε_{ii}) :

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

$$\varepsilon_{ii}/k = \varepsilon_a + \varepsilon_b(T - T_0) + \varepsilon_c[T\ln(T_0/T) + T - T_0]$$

④ Binary parameter (λ_{ij}) :

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

[Hydrogen Bonding Parameters]

- ▣ The segment number of donors and acceptors : $r^H = 0.05$
- ▣ $A_{kl}^{HB} = U_{kl}^{HB} - TS_{kl}^{HB}$

	U_{kl}	S_{kl}
alcohols	$-25.1 \times 10^3 J/mol$	$-26.5 J/mol$
water	$-15.5 \times 10^3 J/mol$	$-16.6 J/mol$

Hydrogen bonding parameters for NLF-HB EOS

III. Comparison of Excess enthalpy using NLF and NLF-HB Theory

▣ System

(1) HEXANE ------------------------ C_6H_{14}
(2) 1-HEXANOL ------------------- $C_6H_{14}O$

▣ Pure component parameters for NLF-HB EOS

Component	γ^a	γ^b	γ^c	ε^a	ε^b	ε^c
n-Hexane	11.469	-1.066E-03	7.080E-03	97.26	2.446E-02	-4.027E-02
1-Hexanol	11.572	2.470E-03	1.081E-02	106.27	3.114E-02	-1.561E-02

▣ Hydrogen bonding parameters for NLF-HB EOS

Component	U^{HB}	S^{HB}
1-Hexanol	-25500 (J/mol)	-26.50 (J/mol K)

(1) HEXANE ---------------------------- C6H14
(2) 1-HEXANOL ------------------------- C6H14O

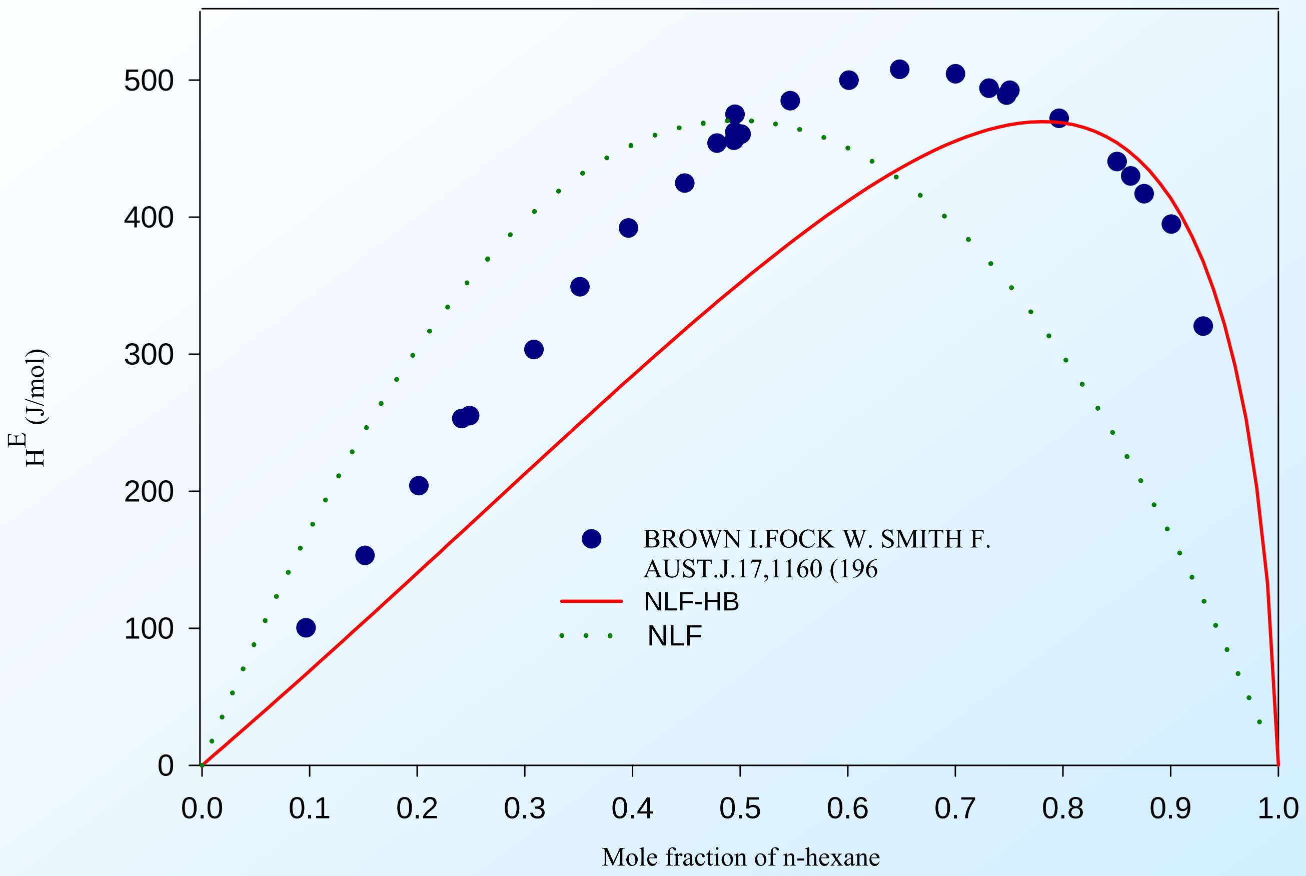
▶ TEMPERATURE = 25.00 deg C (298.15 K)

ref. : BROWN I.,FOCK W.,SMITH F.
AUST.J.CHEM. 17,1106(1964).

X(1)	HE(J/MOL)
0.241400	253.00
0.478500	454.00
0.494500	456.00
0.495100	462.00
0.495400	475.00
0.731400	494.00
0.747700	489.00
0.862900	430.00
0.875500	417.00

ref. : WANG X.,LIU Y.,SUN X.,
THERMOCHIM.ACTA 253,51(1995).

X(1)	HE(J/MOL)	X(1)	HE(J/MOL)
0.096700	100.30	0.601100	499.90
0.151600	153.10	0.648300	507.80
0.201600	204.00	0.700200	504.50
0.248700	255.10	0.750700	492.50
0.308500	303.30	0.796400	472.10
0.351300	349.20	0.850300	440.50
0.396300	392.00	0.900700	394.90
0.448600	428.80	0.930300	320.40
0.500900	460.50		
0.546700	484.90		



Comparison of calculated excess enthalpies (NLF : NLF-HB)
for n-hexane + 1-hexanol system with experimental results

IV. Conclusion

① NLF and NLF-HB Theory is based on the extended Veytsman statistics(1990) and You et al(1994).

② The NLF-HB EOS is better agreements with experimental data than pure physical NLF EOS for associating molecular.

③ The NLF-HB EOS is applied to binary mixtures of water , alcohol, acid , and amine, etc…

④ Simultaneous representation method of VLE and excess enthalpy using NLF-HB EOS is studied and applied to nonpolar + associating components.