The simultaneous prediction of vapor-liquid equilibrium and excess enthalpy

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YOSHINORI ADACHI AND HIDEZUMI SUGIE (1998)

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Kazuo Kojima (1997)

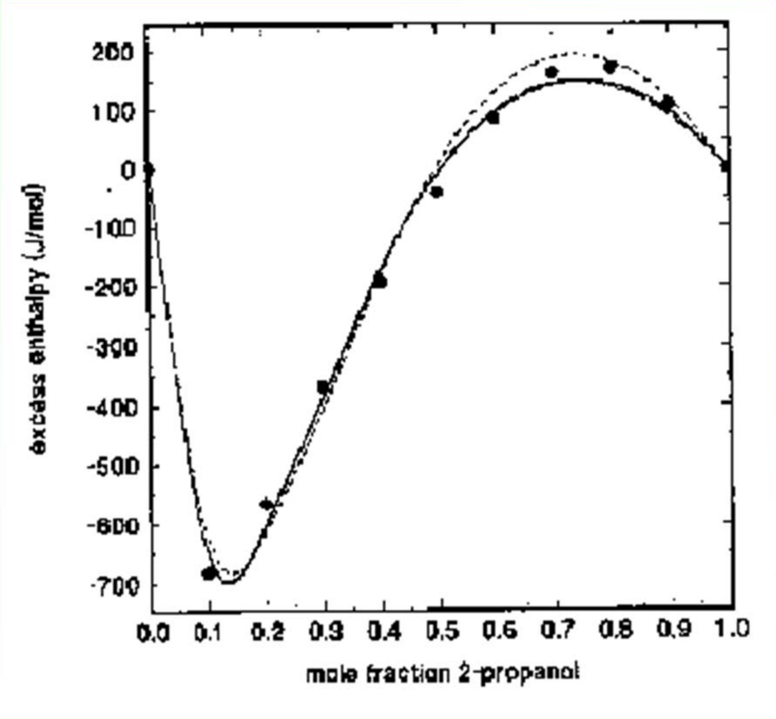
【1】 The simultaneous correlation VLE and H^E

Hasan Orbey , Stanley I. Sandler (1996)

- An attempt to represent simultaneously VLE and H^E behavior

  Non ideal binary mixtures
- Representational method of VLE and H^E
  - ① The activity coefficient model
  - ② Equation of state
- Cubic EOS and various types of mixing rules
  - ⒜ **VLACM** (van Laar activity coefficient) model
  - ⒝ **VDWEOS** (van der Waals EOS) model
  - ⒞ **WSEOS** (Wong – Sandler) model
  - ⒟ **HVOS** (Orbey – Sandler) model

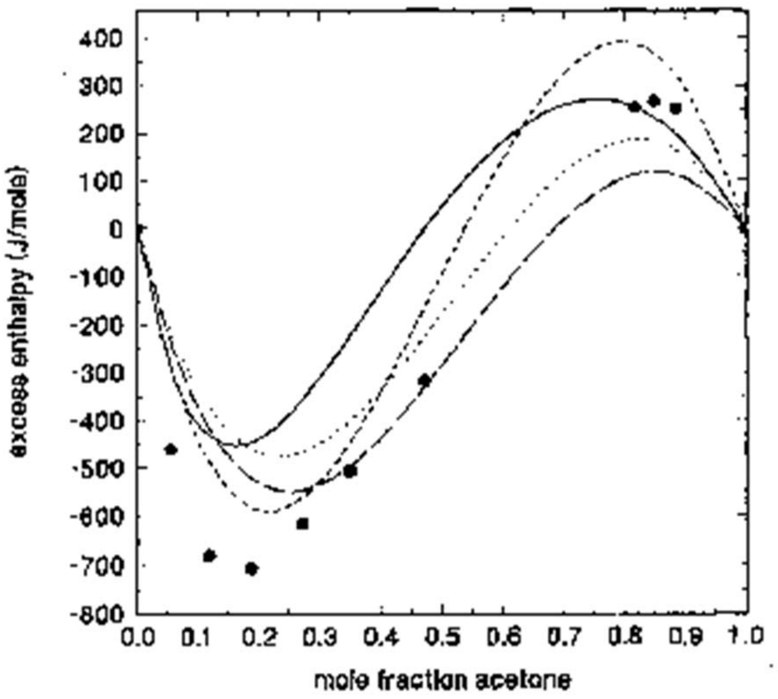
The comparison of models



- Filled circles : Experimental data
- The dotted lines : VLACM
- The solid line : VDWEOS
- The long-dashed line : WSEOS
- The short-dashed line : HVOS

Correlation of the excess enthalpy of 2-propanol + water system at 298.15K

The prediction of VLE and H^E



- Filled circles : Experimental data
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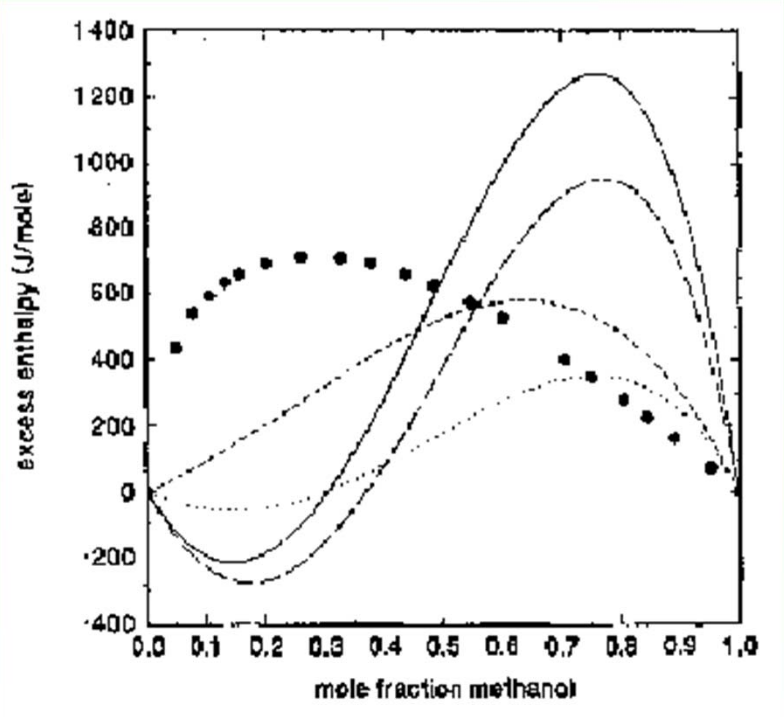
- The long-dashed line : WSEOS
- The short-dashed line : HVOS

Prediction of the excess enthalpy of acetone + water system at 293.15K and 305.15K

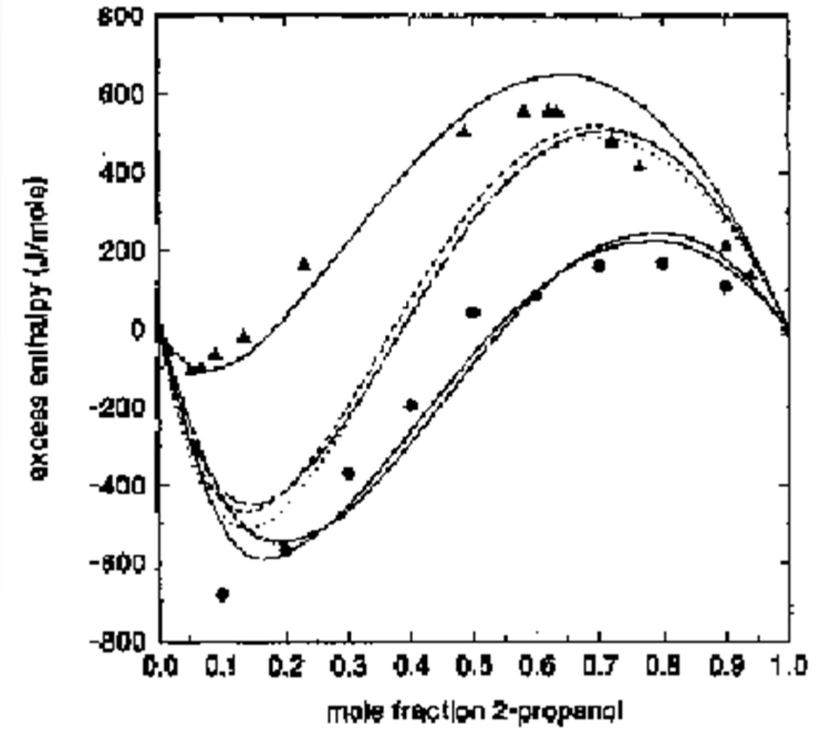
Exception



- Filled circles : Experimental data
- The dotted lines : VLACM
- The solid line : VDWEOS
- The long-dashed line : WSEOS
- The short-dashed line : HVOS

Prediction of the excess enthalpy of the methanol +benzene system at 298.15K with parameters obtained from the correlation of VLE data at 293.15K

The behavior of EOS model



- Filled circles :298.15K data
- Filled triangles : 348.15K data
- The dotted lines : VLACM
- The solid line : VDWEOS
- The long-dashed line : WSEOS
- The short-dashed line : HVOS

Excess enthalpy of 2-propanol+ water system obtained from simultaneous correlation with VLE data at 298.15K, by prediction at 348.15K with the same parameter system at 293.15K and 305.15K

Conclusion

⑴ All of the EOS models are good or better than activity coefficient models for simultaneous correlation and prediction of VLE and H^E properties.

⑵ Fitting parameters used here only to excess enthalpy data or VLE data are compatible but another property did not give satisfactory results.

⑶ The VDWEOS model led to extrapolations of reasonable accuracy for the excess enthalpy and VLE at another temperature.

【2】 Calculation of H^E with the CCOR EOS

H.-M Lin , M.-J Lee (1994)

The Cubic chain - of - rotators (CCOR) equation of state

$$P = \frac{RT[1+0.77(b/V)]}{V-0.42b} + C^R\left[\frac{0.055RT(b/V)}{V-0.42b}\right] - \frac{a}{V(V+c)}$$
$$-\frac{bd}{V(V+C)(V-0.42b)}$$

① The first term

: simplification of the Carnahan-Starling equation for a hard-sphere fluid

② The second term

: contribution to pressure due to the rotational motion of a polyatomic molecule

③ The last two term : the attractive force contributions

CCOR EOS (Lin et al.,1983 ; Kim et al.,1986)

① Applications

: To calculate excess enthalpies for a variety of binary mixtures

② Characteristics

- Non-polar/polar and polar/polar system
- The conditions in both gas and liquid phase

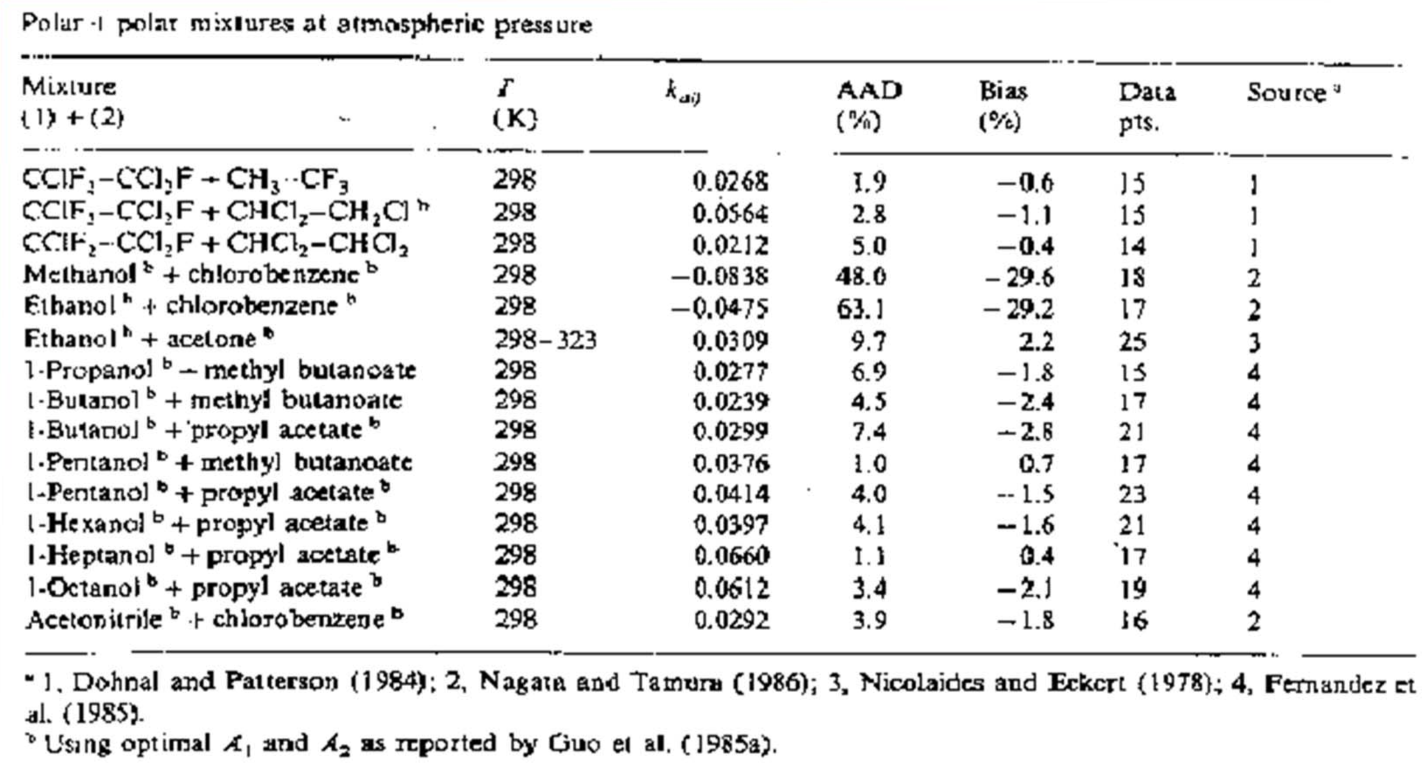
③ Deviations

- Mixtures containing long-chain molecules such as n-hexadecane
- Asymmetric mixture

Exception of CCOR EOS

- System : methanol + chlorobenzene [AAD = 48 %]

  ethanol + chlorobenzene [AAD = 63.1 %]



Polar + polar mixtures at atmospheric pressure

Mixture (1) + (2)	T (K)	k_{aij}	AAD (%)	Bias (%)	Data pts.	Source [a]
$CClF_2-CCl_2F + CH_3-CF_3$	298	0.0268	1.9	−0.6	15	1
$CClF_2-CCl_2F + CHCl_2-CH_2Cl$ [b]	298	0.0564	2.8	−1.1	15	1
$CClF_2-CCl_2F + CHCl_2-CHCl_2$	298	0.0212	5.0	−0.4	14	1
Methanol [b] + chlorobenzene [b]	298	−0.0838	48.0	−29.6	18	2
Ethanol [b] + chlorobenzene [b]	298	−0.0475	63.1	−29.2	17	2
Ethanol [b] + acetone [b]	298–323	0.0309	9.7	2.2	25	3
1-Propanol [b] − methyl butanoate	298	0.0277	6.9	−1.8	15	4
1-Butanol [b] + methyl butanoate	298	0.0239	4.5	−2.4	17	4
1-Butanol [b] + propyl acetate [b]	298	0.0299	7.4	−2.8	21	4
1-Pentanol [b] + methyl butanoate	298	0.0376	1.0	0.7	17	4
1-Pentanol [b] + propyl acetate [b]	298	0.0414	4.0	−1.5	23	4
1-Hexanol [b] + propyl acetate [b]	298	0.0397	4.1	−1.6	21	4
1-Heptanol [b] + propyl acetate [b]	298	0.0660	1.1	0.4	17	4
1-Octanol [b] + propyl acetate [b]	298	0.0612	3.4	−2.1	19	4
Acetonitrile [b] + chlorobenzene [b]	298	0.0292	3.9	−1.8	16	2

[a] 1, Dohnal and Patterson (1984); 2, Nagata and Tamura (1986); 3, Nicolaides and Eckert (1978); 4, Fernandez et al. (1985).

[b] Using optimal A_1 and A_2 as reported by Guo et al. (1985a).

Conclusion

⑴ The CCOR equation was applied to calculate excess enthalpies for a variety of mixtures in both gas and liquid states.

⑵ These systems include polar/non-polar and polar/polar mixtures.

⑶ However, the equation did not work as well for highly asymmetric mixtures.

⑷ The substantial discrepancies between calculated and experimental data were obtained for some system.

【3】The prediction of H^E by mixing rules

YOSHINORI ADACHI AND HIDEZUMI SUGIE (1998)

① The effect of the binary interaction parameters of the modified conventional mixing rules on excess thermodynamic properties of mixture.

② A new method to predict thermodynamic properties of mixtures by means of a cubic EOS.

③ The Modified Conventional Mixing Rules

$$a_m = \sum\sum x_i x_j (1 - k_{ij})(a_i a_j)^{0.5}$$

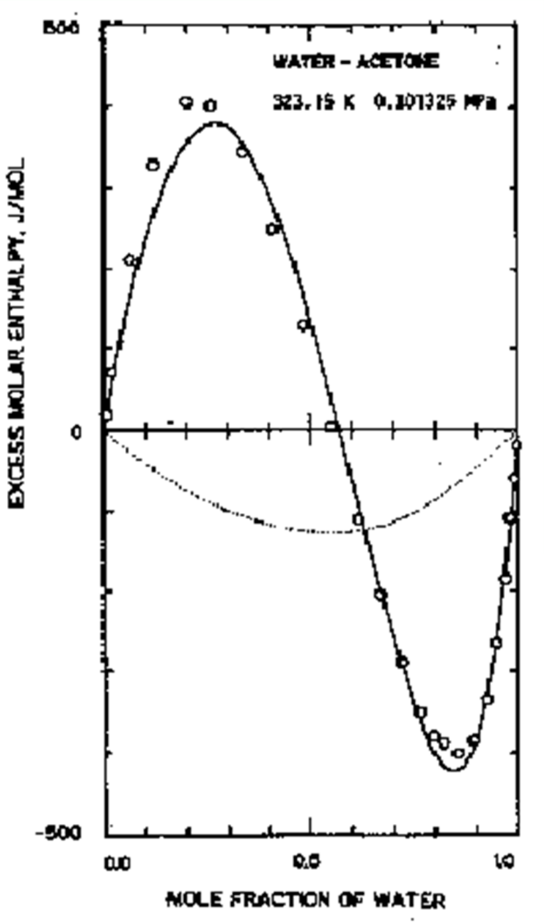
$$\rho^{[illegible]} = \sum x_i \rho^{[illegible]}$$

$$k_{ij} = l_{ij} + m_{ij}(x_i - x_j)$$

④ Excess molar properties

$$M^E = -M' + \sum x_i M'$$

The Modified Conventional Mixing Rule



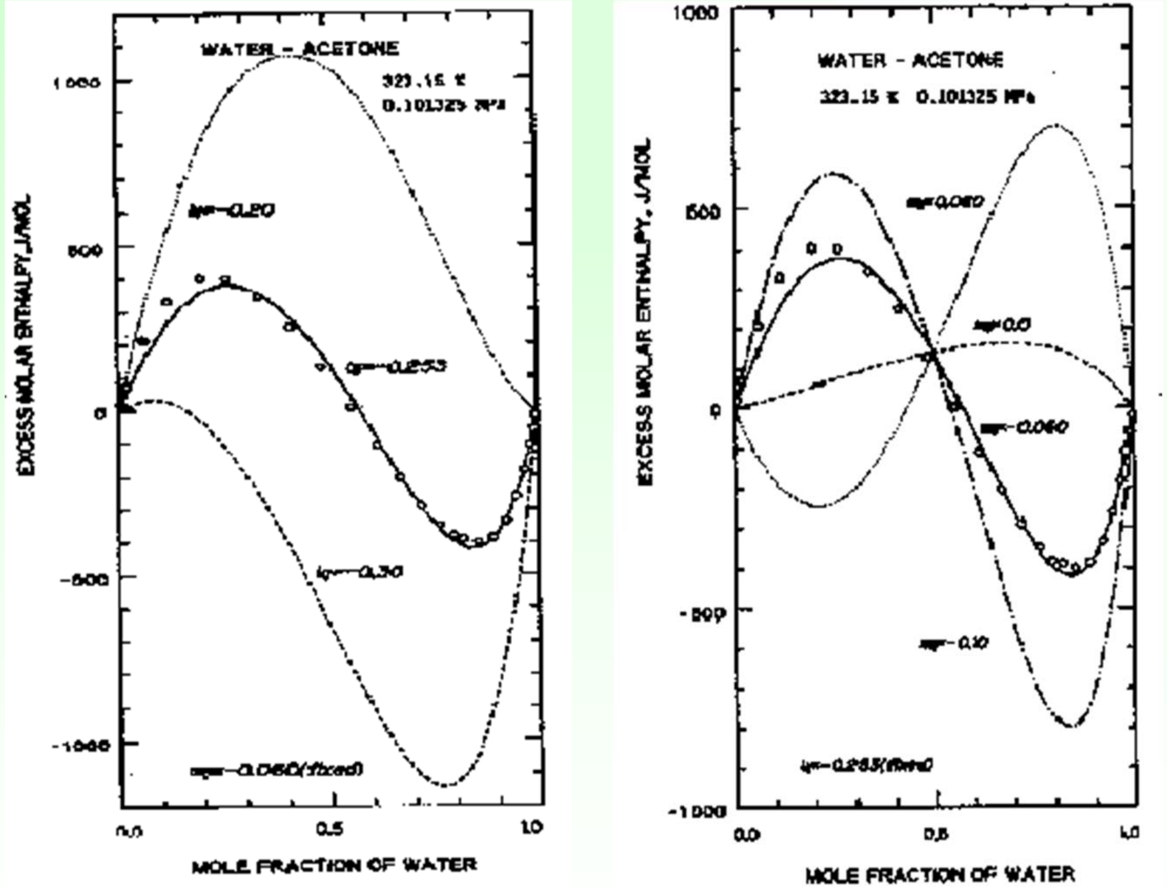
- circles : Experimental data
- ——— : modified conventional mixing rules

  (VDW with l_{ij}=-0.253 and m_{ij}=-0.060)
- - — - : conventional mixing rules

  (VDW with k_{ij}=-0.269)

Excess molar enthalpy of water- acetone system at 323.15K and 0.101325MPa

The effect of binary interaction parameters



* Effect of *l* value on H^E at fixed *m*

* Effect of *m* value on H^E at fixed *l*

l = - 0.253

m = - 0.060

The effect of binary interaction parameter (*l* , *m*) on Excess enthalpy calculation

Conclusion

⑴ The modified conventional mixing rules give satisfactory excess enthalpy and excess volume predictions even for strongly non-ideal solution.

⑵ The calculated result for H^E are more sensitive to the binary interaction parameters than those for V^E.

【4】Group Contribution prediction of VLE and H^E

Kazuo Kojima (1997)

1. VLE calculations
   - At low temperature ⇒ Activity coefficient equations
   - At high temperature ⇒ Equations of state

2. Group Contribution Methods
   - ASOG model, UNIFAC model, …
   - The group interaction parameters can be estimated by regressing available VLE data.

3. The activity coefficient of component *i*

$$\ln \gamma_i = \ln \gamma_i^{COM} + \ln \gamma_i^{RES}$$

① Combinatorial part : the difference in size and shape of molecule

② Residual part : intermolecular force

ASOG model

$$\ln \gamma_i^{COM} = 1 - \frac{S_i}{\sum_j^N S_j x_j} + \ln \frac{S_i}{\sum_j^N S_j x_j}$$

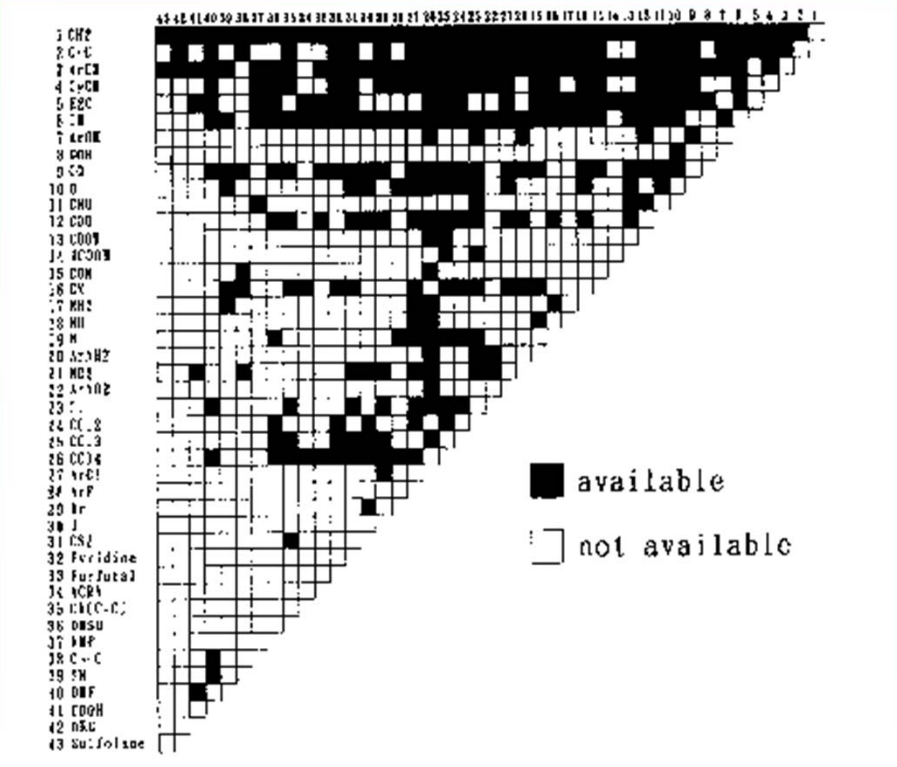
$$\ln \gamma_i^{RES} = \sum_k (\ln \Gamma_k - \ln \Gamma_k^{(i)})$$

$$\ln \Gamma_k = -\ln \sum_{l=1}^m X_l a_{l,k} + (1 - \sum_{l=1}^m \frac{a_{l,k} X_l}{\sum_{i=1}^m a_{i,k} X_i})$$

$$X_l = \frac{\sum_{i=1}^N x_i v_{k,i}}{\sum_{i=1}^N x_i \sum_{I=1}^m v_{l,i}}$$

$$a_{k,l} = \exp(m_{k,l} + \frac{n_{k,l}}{T})$$

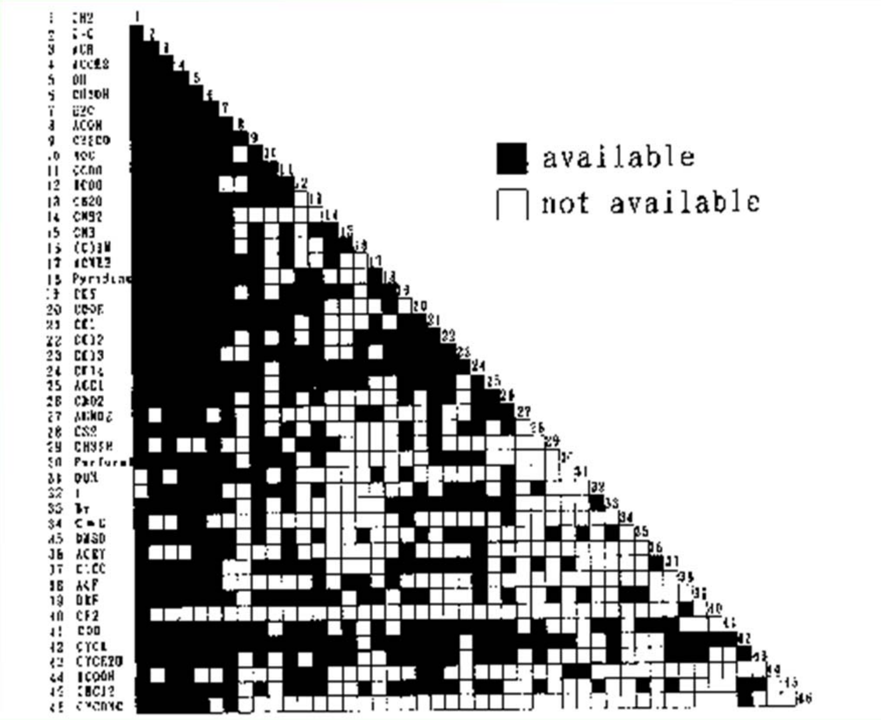
Group interaction parameters



Available ASOG group interaction parameters

[temperature range : 298 ~ 423K]

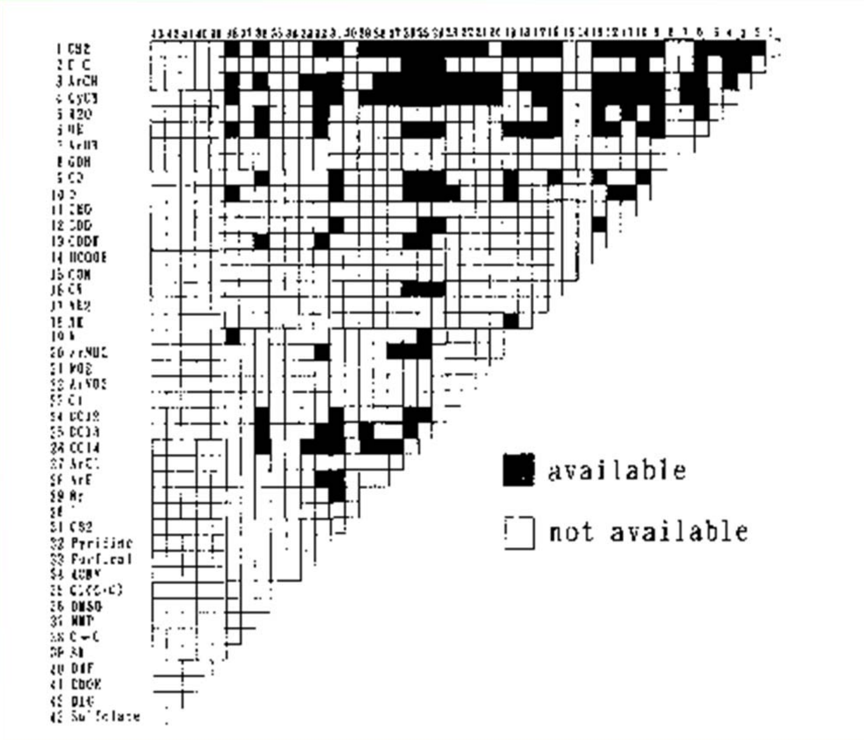
Group interaction parameters



Available modified UNIFAC (Dortmund) group interaction parameters

[temperature range : 293~ 398K]

The ASOG model for predicting the excess enthalpy



Available ASOG-H^E group interaction parameters

[temperature range : 288~ 348K]

Conclusion

⑴ Group contribution methods (ASOG, UNIFAC, modified UNIFAC) for predicting the vapor-liquid equilibrium and the excess enthalpy for mixtures of non-electrolyte solutions are presents.

⑵ Group contribution methods can be used in absence of experimental data.

⑶ The group contribution method have gained widespread popularity in chemical engineering computations.