Estimation of Activity Coefficients by ASOG Group Contribution Method

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Introduction

- Chemical engineering properties of phase equilibria for mixed solutions are essential in separation processes such as distillation, absorption, and extraction.
- When determining the activity coefficients of a non-ideal solution, methods for determining the activity coefficients using information related to atomic groups that compose the molecules without using measured values are called group contribution methods. The ASOG method and the UNIFAC method are representative methods.
- The UNIFAC method is a modified version of the ASOG method, and basically uses the same procedures. Here, we will consider the derivation of the activity coefficients by a group contribution method, by taking the ASOG method as an example.

ASOG(Analytical Solution of Groups) Method

Concept of group contribution methods:

- Generally, a mixture consists of various components.
  The components are composed of various chemical groups, for example, CH2, CH3, OH, CO, COO...
  Accordingly, considering the activity coefficients assigned to the groups in a mixed solution, a method for estimating the activity coefficients of the components by the contributions from the types and numbers of groups included in the chemical formula is called a group contribution method (*) .
- A group contribution method is a model that divides the solution molecules into groups that compose the molecule and estimate the physical properties of the solution by the sum of the interactions between the groups. Process Development Tips Collection 1412 (Lydersen method) and 1601 (Joback Method) are also based on group contribution methods.
- Although the number of components handled in the chemical industry is enormous, the number of groups used as constituting elements of the components is generally about 50 to 100 (the number of basic and important groups is about 50). If the activity coefficient of a component can be determined by group contributions, the activity coefficients of components in mixed solutions that belong to the same types of groups can be widely estimated.

* Kazuo Kojima and Katsumi Tochigi, "ASOG oyobi UNIFAC – Basic ni Yoru Kagaku Kougaku Bussei no Suisan", *in Japanese*: "ASOG and UNIFAC- Estimation of Chemical Engineering Properties by Basic" P12.

Group Solution Models: ASOG Method and UNIFAC Method

- In 1962, Wilson and Deal proposed a semi-theoretical model called the "Group Solution Model" to obtain the activity coefficients of components in a solution by a thermodynamic method. This is said to be the study that became the source for chemical engineering physical property estimation methods (the ASOG and UNIFAC methods) based on the chemical formulas of the components constituting the solutions.
- The ASOG method is a model established by Kojima, Tochigi, et al. of the Nihon University, and uses the Wilson equation to represent the group activity coefficients (it is also possible to express liquid-liquid equilibrium). The term representing the contribution of the molecular size to the activity coefficient is expressed as a function of the number of heavy atoms excluding hydrogen.
- The UNIFAC (Universal Quasichemical Functional-Group Activity Coefficient) method is a model established by Fredenslund, Gmehling, et al., and uses the UNIQUAC equation to represent group activity coefficients. The term representing the contribution of the molecular size to the activity coefficient is expressed using the van der Waals group volume and surface area, respectively.
- Although the UNIFAC method is better known because it has been adopted in process simulators, it is a modified version of the ASOG method and is basically the same.

Estimation of Activity Coefficients by Group Contribution Method

In the case of the ethanol (1) - n-heptane (2) system:

1. Grouping

Ethanol consists of the CH_2 and OH groups, n-heptane is considered to be composed of CH_2 groups. Although both components also contain CH_3, these groups are considered to be equivalent to CH_2 (the same applies for CH). This makes it possible to make predictions with fewer groups.

2. Group Interaction Parameters

The basic factors for determining the activity coefficients of a group are group interaction parameters determined by the group combinations, and these parameters are determined by using vapor-liquid equilibrium data.

3. Estimation of Activity Coefficients

The mixture of ethanol (1) and n-heptane (2) can be considered as a group solution consisting of CH_2 and OH. Knowing the group interaction parameters of CH_2 and OH, it is possible to estimate the activity coefficients of ethanol (1) and n-heptane (2) by group contributions based on their chemical formulas.

Estimation of Activity Coefficients by ASOG method

表3・1　ASOGによる活量係数の推算式

Table 3-1　Equations for Estimating Activity Coefficients by ASOG

$$\ln\gamma_i = \ln\gamma_i^{FH} + \ln\gamma_i^{G} \qquad (3\cdot1)$$

$$\ln\gamma_i^{FH} = \ln\frac{\nu_i^{FH}}{\sum_j x_j \nu_j^{FH}} + 1 - \frac{\nu_i^{FH}}{\sum_j x_j \nu_j^{FH}} \qquad (3\cdot2)$$

$$\ln\gamma_i^{G} = \sum_k \nu_{k,i}(\ln\Gamma_k - \ln\Gamma_k^{(i)}) \qquad (3\cdot3)$$

$$\ln\Gamma_k = -\ln(\sum_i X_i a_{ik}) + 1 - \sum_i \frac{X_i a_{ik}}{\sum_m X_m a_{im}} \qquad (3\cdot4)$$

$$X_k = \frac{\sum_i x_i \nu_{k,i}}{\sum_i x_i \sum_k \nu_{k,i}} \qquad (3\cdot5)$$

$$\ln a_{kl} = m_{kl} + n_{kl}/T \qquad (3\cdot6)$$

γ_i　：混合物中の成分 i の活量係数

$\ln\gamma_i^{FH}$：溶液中の成分分子の大きさによる寄与を表わす項

$\ln\gamma_i^{G}$　：グループ間の相互作用による寄与を表わす項

ν_i^{FH}：純成分 i 中の水素原子を除いた原子の数

$\nu_{k,i}$　：成分 i 中に含まれるグループ k 中の水素原子を除いた原子の総数

γ_i　: Activity Coefficient of Component i in the Mixture

$\ln\gamma_i^{FH}$: Contribution of the Component Molecules in the Solution

$\ln\gamma_i^{G}$: Contribution of Interaction between Groups

ν_i^{FH} : Number of Atoms Excluding Hydrogen Atoms in Pure Component i

$\nu_{k,i}$: Total Number of Atoms Excluding Hydrogen Atoms in Group k Contained

When the activity coefficient of the component i in the solution is γ_i, $\ln(\gamma_i)$ is expressed as the sum of

1. The $\ln(\gamma_i^{FH})$ term: the effect due to the difference in the size of the component molecules and,

2. The $\ln(\gamma_i^{G})$ term: the effect of interactions between groups.

1. The $\ln(\gamma_i^{FH})$ term can be regarded as a function of the number of heavy atoms excluding hydrogen.

2. The $\ln(\gamma_i^{G})$ term is a function of temperature and group interaction parameters $m_{k/l}$, $n_{k/l}$.

* Kazuo Kojima and Katsumi Tochigi, "ASOG oyobi UNIFAC – Basic ni Yoru Kagaku Kougaku Bussei no Suisan", *in Japanese*: "ASOG and UNIFAC- Estimation of Chemical Engineering Properties by Basic" P14.

Reference: Group Activity Coefficients

Representation by Wilson method (general system)

$$\ln(\gamma_i) = 1 - \ln(\sum_j \Lambda_{ji} x_j) - \sum_j \left(\frac{\Lambda_{ji} x_j}{\sum_k \Lambda_{jk} x_k}\right)$$

$$\ln(\Lambda_{ij}) = a_{ij} + \frac{b_{ij}}{T}$$

Two-component system:

$$\ln\gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right)$$

$$\ln\gamma_2 = -\ln(\Lambda_{21}x_1 + x_2) - x_1\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right)$$

$$\ln\gamma_i = \ln\gamma_i^{FH} + \ln\gamma_i^{G} \quad (3\cdot1)$$

$$\ln\gamma_i^{FH} = \ln\frac{\nu_i^{FH}}{\sum_j x_j \nu_j^{FH}} + 1 - \frac{\nu_i^{FH}}{\sum_j x_j \nu_j^{FH}} \quad (3\cdot2)$$

$$\ln\gamma_i^{G} = \sum_k \nu_{k,i}(\ln\Gamma_k - \ln\Gamma_k^{(i)}) \quad (3\cdot3)$$

$$\ln\Gamma_k = -\ln(\sum_l X_l a_{kl}) + 1 - \sum_l \frac{X_l a_{lk}}{\sum_m X_m a_{lm}} \quad (3\cdot4)$$

$$X_k = \frac{\sum_i x_i \nu_{ki}}{\sum_i x_i \sum_k \nu_{ki}} \quad (3\cdot5)$$

$$\ln a_{kl} = m_{kl} + n_{kl}/T \quad (3\cdot6)$$

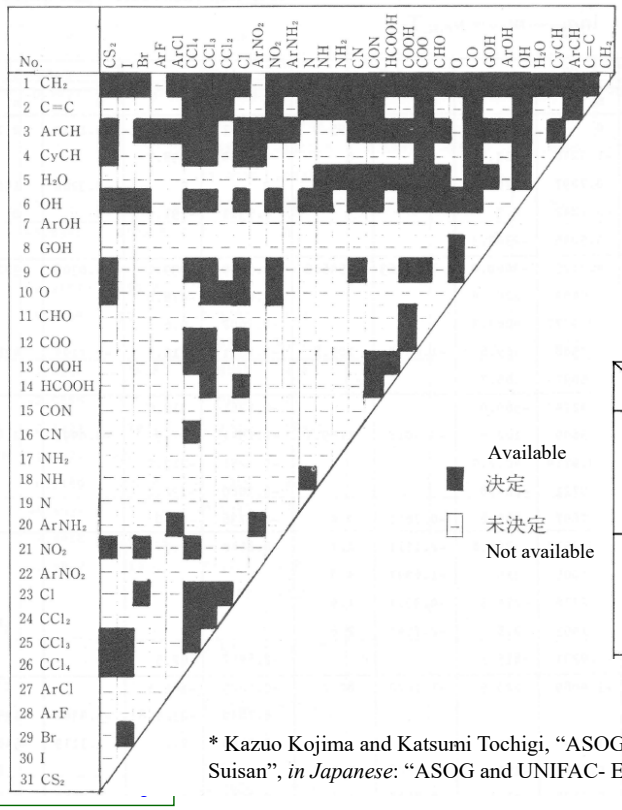
In the case of the ASOG method, it can be seen that the Wilson equation is used as a representation of the group activity coefficients.

The UNIFAC method uses the UNIQUAC equation

ASOG Method Group Interaction Parameters

Table 3-2 ASOG Group Interaction Parameters

表3・2 ASOG グループ対パラメーター



In 1979, 286 of the 31 groups in the table were determined. A theoretical calculation indicates there are 31 × 30 = 930 groups, and there are many undetermined values. The operating temperature range is 303K to 423K.

Table 3-3 ASOG Group Interaction Parameters

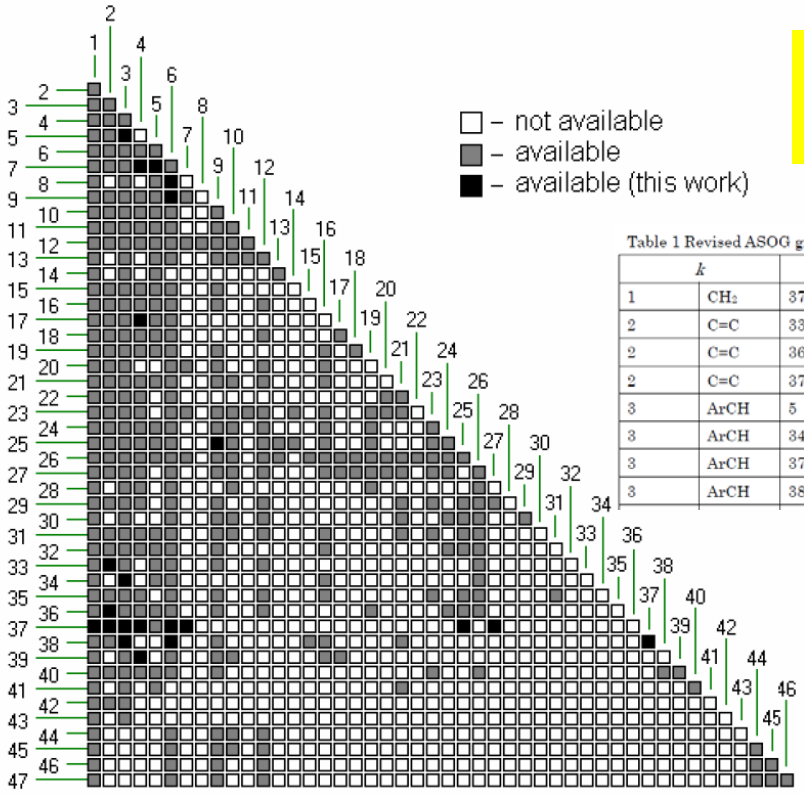
表3・3 ASOG グループ対パラメーター m_{kl}, n_{kl} (303.15K−423.15K)[R8]

$\ln a_{kl} = m_{kl} + n_{kl}/T$

l / k	CH2		C=C		ArCH		CyCH	
	m	n	m	n	m	n	m	n
CH2	0	0	1.3296	-995.0	-0.7457	146.0	0.1530	2.1
C=C	-1.5240	713.8	0	0	-0.5754	338.7		
ArCH	0.7297	-176.8	-1.5842	247.4	0	0	-0.3288	156.3
CyCH	-0.1842	0.3			0.5301	-251.0	0	0
H2O	0.5045	-2382.3						
OH	4.7125	-3060.0	10.5763	-4545.3	-0.5859	-939.1	5.6308	-3221.4
ArOH	3.5403	-2282.8			-2.0123	-478.0		
GOH	-12.9277	4063.3			-0.9602	5.6		
CO	-1.7588	169.6	-1.6404	109.8	-0.4021	-216.8	-2.7194	428.0
O	-0.5097	165.7						

* Kazuo Kojima and Katsumi Tochigi, “ASOG oyobi UNIFAC – Basic ni Yoru Kagaku Kougaku Bussei no Suisan”, *in Japanese*: “ASOG and UNIFAC- Estimation of Chemical Engineering Properties by Basic” P15,16.

ASOG Method Group Interaction Parameters



In a 2011 paper, it was expanded to 46 groups and reported with corrected parameters.

Table 1 Revised ASOG group interaction parameters

k		l		m_{kl}	n_{kl}[K]	m_{lk}	n_{lk}[K]
1	CH_2	37	NMP*	-0.4505	62.5	0.2854	-127.4
2	C=C	33	Furfural*	-0.1147	-47.1	-0.0993	16.7
2	C=C	36	DMSO*	0.3592	-95.8	-0.4881	-41.6
2	C=C	37	NMP*	-1.5635	365.1	2.1023	-639.4
3	ArCH	5	H_2O	-0.0649	-252.4	-2.1939	150.3
3	ArCH	34	ACRY*	0.0965	89.6	-0.5230	-41.6
3	ArCH	37	NMP*	1.0714	-230.2	-1.5972	368.8
3	ArCH	38	$C \equiv C$	0.2346	-46.8	-0.5755	114.2

"Determination of ASOG Parameters – Extension and Revision", Journal of Chemical Engineering of Japan (2011)

Parameters Determined by Chemical Formula (v_i^{FH}, $v_{k,i}$)

v_i^{FH}, $v_{k,i}$ are parameters determined by the chemical formula

v_i^{FH}：純成分 i 中の水素原子を除いた原子の数
$v_{k,i}$：成分 i 中に含まれるグループ k 中の水素原子を除いた原子の総数

Number of Atoms Excluding Hydrogen Atoms in Pure Component i
Total Number of Atoms Excluding Hydrogen Atoms in Group k Contained

For ethanol [CH_3CH_2OH]: Groups k (CH_2: 2 groups, OH: 1 group)

$v_i^{FH} = 3$

$v_{CH2,\,i} = 2$, $v_{OH,\,i} = 1$

However, the coefficients are exceptionally adjusted for CH_2, CH, and C, because the sizes of atomic groups are different. Also, H_2O is defined separately.

$v_{H2O,\,i} = 1.6$, $v_{CH,\,i} = 0.8$, $v_{C,\,i} = 0.5$

For tert-butanol [$(CH_3)_3COH$]: Groups k (CH_2: 3 groups, C: 1 group, OH: 1 group)

$v_i^{FH} = 5$

$v_{CH2,\,i} = 3$, $v_{C,\,i} = 0.5$, $v_{OH,\,i} = 1$

$\therefore v_{CH2,\,i} = 3.5$, $v_{OH,\,i} = 1$

Application Example: Vapor-Liquid Equilibrium Estimation -1

For the ethanol (1) - n-heptane (2) system ($x_1 = 0.241$, $P = 760$ mmHg):

Ethanol (1): $v_1^{FH} = 3$

$v_{CH2,1} = 2,\ v_{OH,1} = 1$

n-heptane (2): $v_2^{FH} = 7$

$v_{CH2,2} = 7$

1. CH2, OH Group Fractions:

$$X_{CH2} = \frac{\sum x_i \cdot v_{CH2,i}}{\sum x_j \cdot v_j^{FH}} = \frac{2x_1 + 7x_2}{3x_1 + 7x_2} = 0.9601$$

$$X_{OH} = \frac{\sum x_i \cdot v_{OH,i}}{\sum x_j \cdot v_j^{FH}} = \frac{x_1 + 0}{3x_1 + 7x_2} = 0.0399$$

2. Group Fractions under Standard Conditions:

$$X_{CH2}^{(1)} = \frac{2x_1}{3x_1} = 0.6667, \quad X_{CH2}^{(2)} = \frac{7x_2}{7x_2} = 1.000$$

$$X_{OH}^{(1)} = \frac{x_1}{3x_1} = 0.3333, \quad X_{OH}^{(2)} = \frac{0}{7x_x} = 0.0000$$

$X_k^{(i)}$: Group Activity Coefficient in Pure Component

Vapor-Liquid Equilibrium Estimation -2

3. Groups Wilson Parameters:

$m_{CH2/OH} = -41.250, n_{CH2/OH} = 7686.4$

$m_{OH/CH2} = 4.7125, n_{OH/CH2} = -3059.9$

Group interaction parameter (From the parameter chart)

$$\ln(a_{k/l}) = m_{k/l} + \frac{n_{k/l}}{T}$$

$$\therefore a_{CH2/OH} = \exp\left(-41.250 + \frac{7686.4}{T}\right)$$

$$a_{OH/CH2} = \exp\left(4.7125 + \frac{-3059.9}{T}\right)$$

4. Group Activity Coefficients:

$$\ln(\Gamma_k) = 1 - \sum\left\{\frac{X_l \cdot a_{l/k}}{\sum X_l \cdot a_{l/m}} - \ln\left(\sum X_l \cdot a_{k/l}\right)\right\}$$

$$\therefore \ln(\Gamma_{CH2}) = 1 - \left(\frac{X_{CH2}}{X_{CH2} + X_{OH} \cdot a_{CH2/OH}} + \frac{X_{OH} \cdot a_{OH/CH2}}{X_{CH2} \cdot a_{OH/CH2} + X_{OH}}\right) - \ln\left(X_{CH2} + X_{OH} \cdot a_{CH2/OH}\right)$$

$$\ln(\Gamma_{OH}) = 1 - \left(\frac{X_{CH2} \cdot a_{CH2/OH}}{X_{CH2} + X_{OH} \cdot a_{CH2/OH}} + \frac{X_{OH}}{X_{CH2} \cdot a_{OH/CH2} + X_{OH}}\right) - \ln\left(X_{CH2} \cdot a_{OH/CH2} + X_{OH}\right)$$

Vapor-Liquid Equilibrium Estimation -3

5. Activity Coefficients:

$$\ln(\gamma_i) = \ln(\gamma_i^{FH}) + \ln(\gamma_i^{G})$$

$$\ln(\gamma_i^{FH}) = \ln\left(\frac{v_i^{FH}}{\sum x_j \cdot v_j^{FH}}\right) + 1 - \frac{v_i^{FH}}{\sum x_j \cdot v_j^{FH}}$$

$$\ln(\gamma_i^{G}) = \sum v_{k,i}\left(\ln(\Gamma_k) - \ln(\Gamma_k^{(i)})\right)$$

$$\therefore \ln(\gamma_1^{FH}) = \ln\left(\frac{3}{3x_1 + 7x_2}\right) + 1 - \frac{3}{3x_1 + 7x_2}$$

$$\ln(\gamma_1^{G}) = 2\left(\ln(\Gamma_{CH2}) - \ln(\Gamma_{CH2}^{(i)})\right) + \left(\ln(\Gamma_{OH}) - \ln(\Gamma_{OH}^{(i)})\right)$$

$$\ln(\gamma_2^{FH}) = \ln\left(\frac{7}{3x_1 + 7x_2}\right) + 1 - \frac{7}{3x_1 + 7x_2}$$

$$\ln(\gamma_2^{G}) = 7\left(\ln(\Gamma_{CH2}) - \ln(\Gamma_{CH2}^{(i)})\right) + 0\left(\ln(\Gamma_{OH}) - \ln(\Gamma_{OH}^{(i)})\right)$$

In the case of constant pressure vapor-liquid equilibrium calculations, if a temperature is assumed, the activity coefficients can be calculated.

Using the obtained activity coefficients, the temperature satisfying the basic vapor-liquid equilibrium equations is determined by iterative calculations.

Vapor-Liquid Equilibrium Estimation -4 (EQUATRAN)

```
// ASOG Vapor-Liquid Equilibrium Calculation
// Group Interaction Parameters
mCH2OH = -41.250; mOHCH2 = 4.7125
nCH2OH = 7686.4; nOHCH2 = -3059.9

// Atomic Number Parameters
vCH2_1 = 2; vOH_1 = 1; vFH_1 = 3
vCH2_2 = 7; vOH_2 = 0; vFH_2 = 7

// 1. Group Fractions
XCH2 = (x1*vCH2_1+x2*vCH2_2)/(x1*vFH_1+x2*vFH_2)
XOH = (x1*vOH_1+x2*vOH_2)/(x1*vFH_1+x2*vFH_2)

// 2. Group Fractions in Standard Conditions
XCH2_1 = (x1*vCH2_1+0*vCH2_2)/(x1*vFH_1+0*vFH_2)
XOH_1 = (x1*vOH_1+0*vOH_2)/(x1*vFH_1+0*vFH_2)
XCH2_2 = (0*vCH2_1+x2*vCH2_2)/(0*vFH_1+x2*vFH_2)
XOH_2 = (0*vOH_1+x2*vOH_2)/(0*vFH_1+x2*vFH_2)

// 3. Group Wilson Parameters
a_CH2OH=exp(mCH2OH + nCH2OH/(t+273.15))
a_OHCH2=exp(mOHCH2 + nOHCH2/(t+273.15))

// 4. Group Activity Coefficients
loge(T_CH2) = 1 - XCH2/(XCH2 + XOH*a_CH2OH)-XOH*a_OHCH2/(XCH2*a_OHCH2 + XOH)-loge(XCH2+XOH*a_CH2OH)
loge(T_OH) = 1 - XCH2*a_CH2OH/(XCH2 + XOH*a_CH2OH)-XOH/(XCH2*a_OHCH2 + XOH)-loge(XCH2*a_OHCH2+XOH)
// Standard Group Activity Coefficients
loge(T1_CH2) = 1 - XCH2_1/(XCH2_1 + XOH_1*a_CH2OH)-XOH_1*a_OHCH2/(XCH2_1*a_OHCH2 + XOH_1)-loge(XCH2_1+XOH_1*a_CH2OH)
loge(T1_OH) = 1 - XCH2_1*a_CH2OH/(XCH2_1 + XOH_1*a_CH2OH)-XOH_1/(XCH2_1*a_OHCH2 + XOH_1)-loge(XCH2_1*a_OHCH2+XOH_1)
loge(T2_CH2) = 1 - XCH2_2/(XCH2_2 + XOH_2*a_CH2OH)-XOH_2*a_OHCH2/(XCH2_2*a_OHCH2 + XOH_2)-loge(XCH2_2+XOH_2*a_CH2OH)
loge(T2_OH) = 1 - XCH2_2*a_CH2OH/(XCH2_2 + XOH_2*a_CH2OH)-XOH_2/(XCH2_2*a_OHCH2 + XOH_2)-loge(XCH2_2*a_OHCH2+XOH_2)
```

Vapor-Liquid Equilibrium Estimation -5 (EQUATRAN)

```
// 5. Activity Coefficients
loge(g1)    = loge(g1_FH) + loge(g1_G)
loge(g1_FH) = loge(vFH_1/(x1*vFH_1 +x2*vFH_2)) + 1 - vFH_1/(x1*vFH_1 +x2*vFH_2)
loge(g1_G)  = vCH2_1*(loge(T_CH2)-loge(T1_CH2)) + vOH_1*(loge(T_OH)-
loge(T1_OH))
loge(g2)    = loge(g2_FH) + loge(g2_G)
loge(g2_FH) = loge(vFH_2/(x1*vFH_1 +x2*vFH_2)) + 1 - vFH_2/(x1*vFH_1 +x2*vFH_2)
loge(g2_G)  = vCH2_2*(loge(T_CH2)-loge(T2_CH2)) + vOH_2*(loge(T_OH)-
loge(T2_OH))

//Input
P = 760
x1 = 0.241

// Vapor-Liquid Equilibrium Calculation
P*y1 = g1*x1*P10
P*y2 = g2*x2*P20

// Sum of Compositions
x1 + x2 = 1
EQ : y1 + y2 = 1

// Vapor Pressures
log10(P10) = 8.16290 - 1623.220/(t + 228.980)
log10(P20) = 6.91740 - 1276.623/(t + 217.838)

// Temperature Assumption
Reset t # 50[0,100] by EQ

// Output Variables
Output g1, g2, t, x1, y1
```

```
// ASOG Vapor-Liquid Equilibrium Calculation

<<   results   >>
g1                =   3.183124
g2                =   1.213365
t                 =   72.29288
x1                =   0.241
y1                =   0.6012901
```

Literature Data (*)

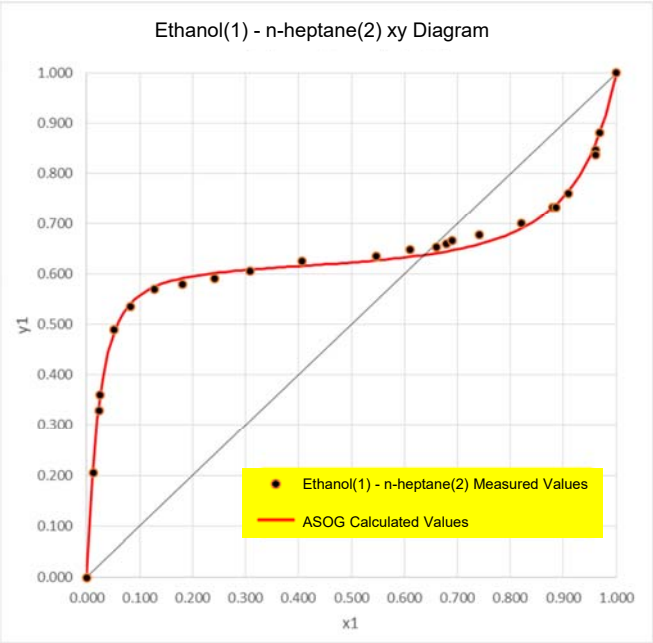
t = 72.4℃

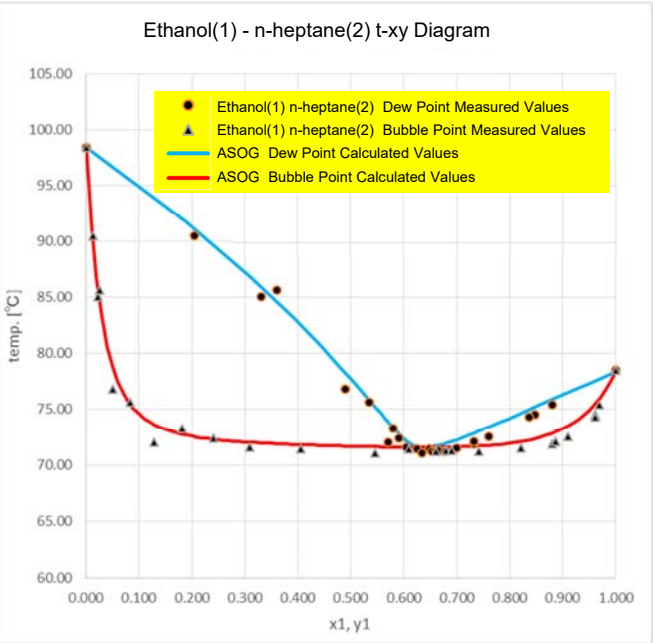
x_1 = 0.241

y_1 = 0.590

* RAAL.J.D, R.K.CODE: J.CHEM.ENG.DATA, Vol.17, 211-216(1972)

Vapor-Liquid Equilibrium Estimation Results - Entire Region Comparison





It can be seen that the estimated values are good.

* RAAL.J.D, R.K.CODE: J.CHEM.ENG.DATA, Vol.17, 211-216(1972)

Group Interaction Parameter Determination

The following objective function was used for determining the parameters:

$$F_{obj.} = W_1 \sum_{i=1}^{2} \left(\ln \gamma_{i,\exp.} - \ln \gamma_{i,cal.} \right)^2 + W_2 \sum_{i=1}^{2} \left(\ln \gamma^{\infty}_{i,\exp.} - \ln \gamma^{\infty}_{i,cal.} \right)^2 \qquad (7)$$

The simplex Nelder and Mead method (1965) was used to obtain the minimum value of $F_{obj.}$ In Eq.(7) W_1 and W_2 are, respectively, the weighting factors that depend on the numbers of data points of VLE and γ^{∞}. As a rule, we adopted 5 for W_1 and 1 for W_2.

The group interaction parameters are obtained by weighting the data of the vapor-liquid equilibrium measurement values (activity coefficients) and the infinite dilution activity coefficients.

=> The group interaction parameters that have not been reported can be determined by each user.

"Determination of ASOG Parameters - Extension and Revision", Journal of Chemical Engineering of Japan (2011)

Conclusion

- Calculations were performed with regard to group contribution methods for determining activity coefficients using information on the atomic groups that compose molecules, by using the ASOG method as an example.
- In the ASOG method, activity coefficients are expressed as the sum of the γ_i^{FH} term: the effect of the difference in the sizes of component molecules, and the γ_i^{G} term: the effect of interaction between groups.
  The γ_i^{FH} term is expressed by the number of atoms constituting the molecules, and the γ_i^{G} term is expressed using the Wilson equation.
- The group Wilson parameters are required to estimate activity coefficients, and they are a function of group interaction parameters and temperature.
  In other words, the group interaction parameters are not a function of temperature.
- Since group interaction parameters can be determined by the least squares method using measured data, parameters can be derived even for unreported groups, and this will extend the possible ranges of estimation.