

Prediction of Vapor-Liquid Equilibria of Binary Systems Consisting of Homogeneous Components by Using Wilson Equation with Parameters Estimated from Pure-Component Properties

Shigetoshi KOBUCHI, Kei TAKAKURA

(Department of Environmental Science and Engineering, Graduate School of Science and Engineering, Yamaguchi University)

Setsuko YONEZAWA (Department of Chemical Engineering, Faculty of Engineering, Kyushu University)

Kenji FUKUCHI (Department of Chemical and Biological Engineering, Ube National College of Technology)

Yasuhiko ARAI (Professor Emeritus of Kyushu University)

A simple method previously proposed for estimating Wilson parameters on the basis of solubility parameters and molar volumes given from group-contribution methods and normal boiling points of pure substances has been adopted to predict the vapor-liquid equilibria of binary systems consisting of homogeneous components. The prediction performances are examined and discussed.

Keywords: *Wilson Parameter, Vapor-Liquid Equilibrium, Prediction, Binary System, Homogeneous Component, Solubility Parameter, Molar Volume, Pure-Component Property*

Introduction

According to a simple model GC-W (Group-Contribution method based Wilson equation) previously proposed in a series of our studies¹⁻⁷⁾, the Wilson parameters⁸⁾ A can be estimated as follows from molar volumes v and solubility parameters δ which can be easily given by group contribution methods.

$$A_{ij} = \frac{v_j}{v_i} \exp \left[-\frac{\lambda_{ij} - \lambda_{ii}}{RT} \right] \quad (1)$$

where λ_{ij} denotes the interaction energy due to attractive force between i and j molecules and given by;

$$\lambda_{ij} = -(1 - \varepsilon_{ij})(v_i v_j)^{0.5} \delta_i \delta_j; \quad \varepsilon_{ij} = 0 \quad (i = j) \quad (2)$$

The interaction parameters between unlike molecules ε_{12} and ε_{21} in Eq. (2) have been evaluated from reliable VLE (Vapor-Liquid Equilibria) data given in the literature with good correlation performances for various non-polar and polar binary systems. Those

interaction parameters obtained have been approximated by the empirical equations proposed by the previous studies to predict VLE from pure-component properties such as solubility parameters δ and normal boiling points t_b .

1. Interaction Parameters for Homogeneous Mixtures

In this study, as an extension, the GC-W model has been adopted to predict VLE of binary systems consisting of homogeneous components and its prediction performances are examined and discussed. For a homogeneous binary system, the following two conventional approaches may be considered. For a non-polar or slightly polar homogeneous binary system such as paraffinic hydrocarbon (1) + paraffinic hydrocarbon (2), the molecular interactions may be quite similar so that $\lambda_{12} = \lambda_{11}$ and $\lambda_{21} = \lambda_{22}$ seems to be valid. In this case, the interaction parameters ε_{12} and ε_{21} can be derived as follows from Eq. (2).

$$\varepsilon_{12}(\text{FH}) = 1 - \left(\frac{v_1}{v_2}\right)^{0.5} \frac{\delta_1}{\delta_2} \quad (3)$$

$$\varepsilon_{21}(\text{FH}) = 1 - \left(\frac{v_2}{v_1}\right)^{0.5} \frac{\delta_2}{\delta_1} \quad (4)$$

where the averaged temperature $t(\text{avg.}) = (t_{b,1} + t_{b,2})/2$ is adopted as an approximation to calculate molar volumes and solubility parameters. When Eqs. (3) and (4) are applied, the Wilson equation is reduced to the Flory-Huggins (FH) equation⁹⁾. On the other hand, for a polar homogeneous binary system, alcohol (1) + alcohol (2) for example, an approximation by the ideal solution model may be rather acceptable because the molecular interaction effect (the heat of mixing term) may be cancelled by the excess entropy effect. In this approximation ($\gamma_1=1$ and $\gamma_2=1$), the Wilson parameters become to $A_{12}=1$ and $A_{21}=1$. From these conditions, the interaction parameters ε_{12} and ε_{21} can be derived as follows from Eqs. (1) and (2).

$$\varepsilon_{12}(\text{Ideal}) = 1 - \frac{v_1 \delta_1^2 - RT \ln(v_2/v_1)}{(v_1 v_2)^{0.5} \delta_1 \delta_2} \quad (5)$$

$$\varepsilon_{21}(\text{Ideal}) = 1 - \frac{v_2 \delta_2^2 - RT \ln(v_1/v_2)}{(v_2 v_1)^{0.5} \delta_2 \delta_1} \quad (6)$$

where $t(\text{avg.})$ mentioned above is adopted.

2. Results and Discussion

The applicabilities of Eqs. (3) and (4) or Eqs. (5) and (6) have been examined by applying them to predict VLE of various non-polar, slightly polar and polar homogeneous binary systems. The pure-component properties required are listed in **Table 1**, except for the other components presented in the previous papers^{4,12)}. The prediction performances obtained are presented in **Table 2** in comparison with those from VLE data fitting. Further, typical illustrations are given by **Figures 1** and **2**. As shown in Table 2, for hydrocarbon, ether, ketones and ester binary systems, good prediction performances are obtained by

using Eqs. (3) and (4) or Eqs. (5) and (6) of which performances are almost same as those from VLE data fitting. It is shown that the prediction performances obtained by Eqs. (3) and (4) are comparable to those by Eqs. (5) and (6). On the other hand, for alcohol binary systems, Eqs. (5) and (6) seem to be better than Eqs. (3) and (4) though their prediction performances are somewhat less than those from VLE data fitting as presented in Table 2. Therefore, the interaction parameters ε_{12} and ε_{21} determined by VLE data fitting have been approximated by the previously proposed equations¹⁾ with t_b and δ_{25} ²⁾ and then the equations have been applied to predict VLE. Nevertheless, the prediction performances obtained are found to be inferior to those by Eqs. (5) and (6). In the previous study⁷⁾, carboxylic acid (1) + carboxylic acid (2) binary systems have been examined and good correlation results are obtained. However, it is noted that the prediction of VLE by Eqs. (3) and (4) or Eqs. (5) and (6) are found to be hard because the carboxylic acid binary systems deviate apparently from the ideal solution behavior. As discussed above, the present GC-W model with Eqs. (5) and (6) can be recommended to predict VLE of binary systems consisting of homogeneous components except carboxylic acid binary systems.

Conclusion

The interaction parameters between unlike molecules ε_{12} and ε_{21} contained in GC-W have been derived for homogeneous mixtures based on the conventional approaches; the Flory-Huggins equation and the ideal solution model. By using the reliable VLE data cited from the literature, the prediction performances of those approaches have been evaluated. It can be recommended to adopt $\varepsilon_{12}(\text{Ideal})$ and $\varepsilon_{21}(\text{Ideal})$ given by Eqs.(5) and (6) for predicting VLE of homogeneous mixtures such as hydrocarbon (1) + hydrocarbon (2) and alcohol (1) + alcohol (2) except carboxylic acid binary systems. The VLE of binary systems consisting of

Table 1 Physical properties of pure substances

Substance	v_{25} [cm ³ ·mol ⁻¹]	v_b [cm ³ ·mol ⁻¹]	δ_{25} [(J·cm ⁻³) ^{0.5}]	t_b [°C]	Constants of Antoine's equation*		
					A	B	C
2-Methyl-2-butanol	107.4	125.8	21.6	102.0 ¹⁰⁾	5.64418	863.400	137.850 ¹⁰⁾
2-Methyl-1-butanol	108.2	125.8	22.0	129.863 ¹¹⁾	9.31613	3517.923	-78.208 ¹¹⁾
3-Methyl-1-butanol	108.2	125.8	22.0	130.5 ¹⁰⁾	6.07849	1128.190	126.68 ¹⁰⁾
Ethyl propyl ketone	126.1	140.6	18.2	123.506 ¹¹⁾	6.12535	1366.067	65.057 ¹¹⁾
1-Octanol	156.2	192.4	21.0	195.160 ¹¹⁾	5.87970	1260.554	142.920 ¹¹⁾

$$*\log p^\circ [\text{kPa}] = A - \{B/(T[\text{K}] - C)\}$$

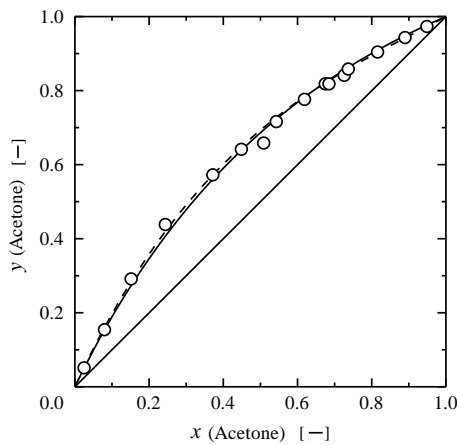


Fig.1 Calculation of VLE for acetone (1) + methyl ethyl ketone (2) at 101.3 kPa: Experimental, (○); Prediction, (—) by Eqs. (3) and (4); Correlation, (-----) by VLE data fitting

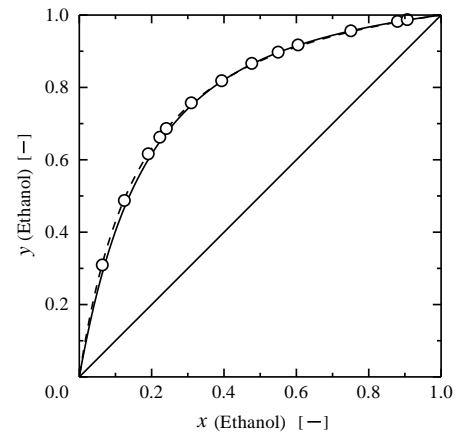


Fig.2 Calculation of VLE for ethanol (1) + 2-methyl-1-butanol (2) at 101.3 kPa: Experimental, (○); Prediction, (—) by Eqs. (5) and (6); Correlation, (-----) by VLE data fitting

homogeneous components studied here can be essentially predicted by adopting Raoult's law or the Flory-Huggins equation. In this case, the Wilson equation is not required. However, it is interesting to understand how the interaction parameters between unlike molecules ε_{12} and ε_{21} should be expressed by using the pure-component properties to reduce GC-W to the ideal solution or the athermal solution model. We can see what values of ε_{12} and ε_{21} of GC-W resemble an ideal solution or an athermal solution.

Nomenclature

p°	= vapor pressure of pure component	[Pa]
R	= gas constant	[J·mol ⁻¹ ·K ⁻¹]
T	= absolute temperature	[K]
t	= temperature	[°C]
v	= liquid molar volume	[cm ³ ·mol ⁻¹]
x	= mole fraction of liquid phase	[-]
y	= mole fraction of vapor phase	[-]
A	= Wilson parameter	[-]
δ	= solubility parameter	[(J·cm ⁻³) ^{0.5}]

Table 2 Prediction performances for VLE of homogeneous binary systems at 101.3kPa

Binary system (1) + (2)	Ref.	N	Eqs. (3) and (4)				Eqs. (5) and (6)				VLE data fitting					
			ε_{12}	ε_{21}	Δy_1^*	Δt^*	ε_{12}	ε_{21}	Δy_1^*	Δt^*	ε_{12}	ε_{21}	Δy_1^*	Δt^*		
Hydrocarbon binary system																
Hexane + Heptane ^b	13	17	0.0795	-0.0863	0.4	0.2	0.0902	-0.0971	0.4	0.1	0.0552	-0.0589	0.7	0.4 ^a		
Heptane + Octane ^c	14	20	0.0730	-0.0787	1.8	0.3	0.0822	-0.0880	1.7	0.3	0.0618	-0.0595	1.7	0.2 ^a		
Benzene + Toluene	15	21	0.0559	-0.0593	1.4	0.4	0.0727	-0.0760	1.7	0.5	0.0851	-0.0884	1.5	0.4 ^a		
Ethylbenzene + <i>p</i> -Xylene ^d	16	11	-0.0066	0.0065	1.2	0.1	-0.0068	0.0068	1.2	0.1	0.0044	-0.0044	1.1	0.1 ^a		
				Avg.	1.2	0.3			Avg.	1.3	0.3			Avg.	1.3	0.3
Ether binary system																
MTBE ^e + TAME ^f	17	28	0.1116	-0.1256	1.2	0.1	0.1224	-0.1364	1.1	0.1	0.1721	-0.1753	1.1	0.2		
Ketone binary system																
Acetone + MEK ^g	18	16	0.1230	-0.1402	1.2	0.5	0.1429	-0.1601	2.3	0.5	0.0839	-0.0613	2.3	0.3		
Acetone + DEK ^h	19	16	0.1783	-0.2171	3.5	0.9	0.2158	-0.2545	2.7	0.6	0.1304	-0.0592	2.1	0.9		
MEK ^g + DEK ^h	18	14	0.0550	-0.0582	1.4	0.3	0.0728	-0.0761	1.4	0.2	0.0728	-0.0761	1.4	0.2		
DEK ^h + MPK ⁱ	19	12	0.0001	-0.0001	0.4	0.3	0.0001	-0.0001	0.4	0.3	0.0406	-0.0317	0.4	0.2		
DEK ^h + EPK ^j	18	10	0.0543	-0.0574	0.5	0.2	0.0678	-0.0709	0.4	0.2	0.0678	-0.0709	0.4	0.2		
DEK ^h + MIBK ^k	18	19	0.0320	-0.0331	2.1	0.2	0.0463	-0.0473	2.3	0.3	0.1558	-0.1212	0.9	0.5		
				Avg.	1.5	0.4			Avg.	1.6	0.4			Avg.	1.3	0.4
Ester binary system																
Methyl formate+Propyl acetate	20	8	0.2439	-0.3225	1.7	1.3	0.3109	-0.3896	1.8	2.0	0.4435	-0.4916	1.6	1.3		
Ethyl formate+Methyl acetate	21	9	-0.0395	0.0380	0.8	0.4	-0.0408	0.0393	0.8	0.4	-0.0470	0.0451	0.8	0.3		
Propyl formate+Propyl acetate	20	12	0.0722	-0.0778	2.9	0.5	0.0875	-0.0931	3.2	0.3	0.0083	0.0707	2.7	0.8		
Butyl formate+Butyl acetate	21	14	0.0690	-0.0741	2.5	0.7	0.0811	-0.0862	2.5	0.8	0.0811	-0.0862	2.5	0.8		
Methyl acetate+Ethyl acetate	21	9	0.1128	-0.1272	2.0	0.5	0.1356	-0.1499	2.4	0.3	0.0967	-0.0988	2.7	0.2		
Ethyl acetate+Butyl acetate	20	13	0.1115	-0.1255	1.1	0.6	0.1395	-0.1535	1.0	0.4	0.1395	-0.1535	1.0	0.4		
				Avg.	1.8	0.7			Avg.	2.0	0.7			Avg.	1.9	0.6
Alcohol binary system																
Methanol + Ethanol	22	11	0.1010	-0.1124	1.7	0.2	0.1318	-0.1431	0.3	0.1	0.1602	-0.1686	0.4	0.0		
Methanol + 1-Propanol	23	19	0.1514	-0.1784	3.6	1.3	0.2016	-0.2287	0.7	0.3	0.1838	-0.2035	0.2	0.0		
Methanol + <i>t</i> -Butanol	23	14	0.1359	-0.1572	3.1	0.5	0.2057	-0.2271	5.2	1.2	0.1303	-0.1256	1.3	0.2		
Methanol + 1-Octanol	22	23	0.3128	-0.4551	16.4	12.6	0.4220	-0.5643	6.0	4.0	0.3684	-0.2948	2.1	3.2		
Ethanol + 2-Propanol	24	11	0.0315	-0.0325	0.9	0.1	0.0512	-0.0523	0.7	0.2	0.0676	-0.0691	0.8	0.1		
Ethanol + <i>t</i> -Butanol	24	28	0.0343	-0.0356	0.4	0.0	0.0721	-0.0734	2.1	0.5	0.0343	-0.0340	0.2	0.0		
Ethanol + 2-Methyl-1-butanol	24	13	0.1129	-0.1272	3.7	2.5	0.1615	-0.1759	1.1	1.1	0.2173	-0.2103	0.6	0.4		
Ethanol + 1-Octanol	24	23	0.2271	-0.2938	10.7	6.1	0.3014	-0.3681	4.6	1.6	0.2455	-0.1581	1.9	2.6		
2-Propanol + <i>i</i> -Butanol	25	9	0.0435	-0.0455	1.6	0.2	0.0591	-0.0611	1.4	0.2	0.0612	-0.0632	1.4	0.2		
<i>t</i> -Butanol + <i>i</i> -Butanol	25	14	0.0470	-0.0494	0.6	0.2	0.0438	-0.0461	0.6	0.2	0.0378	-0.0412	0.6	0.2		
<i>i</i> -Butanol + 1-Butanol	26	17	0.0245	-0.0251	0.6	0.3	0.0236	-0.0242	0.6	0.3	0.0248	-0.0248	0.7	0.3		
2-Methyl-2-butanol + 1-Pentanol	26	14	0.0699	-0.0717	4.9	0.5	0.0628	-0.0676	3.9	0.3	0.1099	-0.1109	1.9	0.6		
3-Methyl-1-butanol + 1-Pentanol	26	12	0.0199	-0.0203	0.7	0.2	0.0192	-0.0196	0.7	0.2	0.0199	-0.0202	0.7	0.2		
				Avg.	3.8	1.9			Avg.	2.1	0.8			Avg.	1.0	0.6

$$* \Delta y_1[\%] = \frac{100}{N} \sum \frac{|y_{1,calc} - y_{1,exp}|}{y_{1,exp}}, \quad \Delta t[^\circ\text{C}] = \frac{1}{N} \sum |t_{calc} - t_{exp}|, \quad N = \text{number of data points}$$

^a The values of ε_{12} and ε_{21} and deviations cited from the previous paper ²⁾, ^b 101.0kPa, ^c 94.0kPa, ^d 100.65kPa, ^e Methyl *t*-butyl ether, ^f *t*-Amyl methyl ether, ^g Methyl ethyl ketone, ^h Diethyl ketone, ⁱ Methyl propyl ketone, ^j Ethyl propyl ketone, ^k Methyl *i*-butyl ketone

ε = interaction parameter between unlike molecules [-]
 λ = interaction energy due to attractive force [$\text{J} \cdot \text{mol}^{-1}$]

<Subscript>

b = normal boiling point
 calc = calculated value
 exp = experimental data
 1 = component 1
 2 = component 2

Literature Cited

- 1) Kobuchi, S., K. Ishige, S. Yonezawa, K. Fukuchi and Y. Arai; "Correlation of Vapor-Liquid Equilibria of Polar Mixtures by Using Wilson Equation with Parameters Estimated from Solubility Parameters and Molar Volumes," *J. Chem. Eng. Japan*, Vol. 44, pp. 449-454, 2011
- 2) Kobuchi, S., K. Ishige, S. Yonezawa, K. Fukuchi and Y. Arai; "Correlation of Vapor-Liquid Equilibria Using Wilson Equation with Parameters Estimated from Solubility Parameters and Molar Volumes," *Mem. Fac. Eng., Yamaguchi Univ.*, Vol. 62, pp. 1-11, 2011
- 3) Kobuchi, S., K. Ishige, K. Takakura, S. Yonezawa, K. Fukuchi and Y. Arai; "Prediction of Vapor-Liquid Equilibria for ETBE+Ethanol, ETBE + Octane, Ethanol + Octane, and ETBE + Ethanol + Octane Systems by the Wilson Equation," *Kagaku Kogaku Ronbunshu*, Vol. 38, pp. 76-79, 2012
- 4) Kobuchi, S., K. Ishige, K. Takakura, S. Yonezawa, K. Fukuchi and Y. Arai; "Correlation of Vapor-Liquid Equilibria of Alcohol + Aliphatic Chloride Binary Systems by Using Wilson Equation with Parameters Estimated from Solubility Parameters and Molar Volumes," *J. Chem. Eng. Japan*, Vol. 45, pp. 311-314, 2012
- 5) Kobuchi, S., K. Ishige, K. Takakura, S. Yonezawa, K. Fukuchi and Y. Arai; "Prediction of Vapor-Liquid Equilibria of Alcohol + Hydrocarbon Binary Systems by Using Wilson Equation with Parameters Estimated from Pure-Component Properties," *J. Chem. Eng. Japan*, Vol. 45, pp. 893-895, 2012
- 6) Kobuchi, S., K. Takakura, S. Yonezawa, K. Fukuchi and Y. Arai; "Estimation of Wilson Parameters from Molecular Structures and Pure-Component Properties," *Proc. 6th Int. Symp. Mol. Thermodyn. Mol. Simul. (MTMS'12)*, Higashi-Hiroshima, Japan, 2012
- 7) Kobuchi, S., K. Takakura, S. Yonezawa, K. Fukuchi and Y. Arai; "Correlation of Vapor-Liquid Equilibria of Binary Systems Containing Carboxylic Acid by Using Wilson Equation with Parameters Estimated from Pure-Component Properties," *J. Chem. Eng. Japan*, Vol. 46, pp. 100-106, 2013
- 8) Wilson, G. M.; "Vapor-Liquid Equilibrium. XI. A New Expression for the Excess Free Energy of Mixing," *J. Am. Chem. Soc.*, Vol. 86, pp. 127-130, 1964
- 9) Hildebrand, J. H., J. M. Prausnitz and R. L. Scott; *Regular and Related Solutions*, Capt. 7, Van Nostrand Reinhold Co., New York, U. S. A., 1970
- 10) Tamir, A and J. Wisniak; "Binary Vapor-Liquid Equilibria of Some Amyl Alcohols," *J. Chem. Eng. Data*, Vol. 21, pp. 182-185, 1976
- 11) Boublik, T., V. Fried and E. Hála; *The Vapour Pressures of Pure Substances*, 2nd ed., Elsevier, Amsterdam, the Netherlands, 1984
- 12) Kobuchi, S., K. Honda, T. Watanabe, S. Yonezawa, K. Fukuchi and Y. Arai; "Correlation of Vapor-Liquid Equilibria for Binary Systems Containing Polar Substances by Regular Solution Model," *Bunrigijutu*, Vol. 40, pp. 250-259, 2010
- 13) Jan, D. -S., H. -Y. Shiau and F. -N. Tsai; "Vapor-Liquid Equilibria of *n*-Hexane + Cyclohexane + *n*-Heptane and the Three Constituent Binary Systems at 101.0kPa," *J. Chem. Eng. Data*, Vol. 39, pp. 438-440, 1994
- 14) Wisniak, J., G. Embon, R. Shafir, H. Segura and R. Reich; "Isobaric Vapor-Liquid Equilibria in the Systems Methyl 1,1-Dimethylethyl Ether + Octane and Heptane + Octane," *J. Chem. Eng. Data*, Vol. 42, pp. 1191-1194, 1997
- 15) Michishita, T., Y. Arai and S. Saito; "Vapor-Liquid Equilibria of Hydrocarbons at Atmospheric Pressure," *Kagaku Kogaku*, Vol. 35, pp. 111-116, 1971
- 16) Rodrigues, W. L., S. Mattedi and J. C. N. Abreu; "Vapor-Liquid Equilibria Data for Binary Systems of Ethylbenzene + Xylene Isomers at 100.65 kPa," *J. Chem. Eng. Data*, Vol. 50, pp. 1134-1138, 2005
- 17) Gmehling, J. and U. Onken; *Vapor-Liquid*

- Equilibrium Data Collection, Ethers: (Supplement 2), DECHEMA Chemistry Data Series, Vol.1, Part 4b, DECHEMA, Frankfurt/Main, Germany, 1999
- 18) Gmehling, J., U. Onken and W. Arlt; Vapor-Liquid Equilibrium Data Collection, Aldehydes and Ketones, Ethers, DECHEMA Chemistry Data Series, Vol. 1, Part 3+4, DECHEMA, Frankfurt/Main, Germany, 1979
- 19) Gmehling J. and U. Onken; Vapor-Liquid Equilibrium Data Collection, Aldehydes and Ketones (Supplement 2), DECHEMA Chemistry Data Series, Vol.1, Part 3c, DECHEMA, Frankfurt/Main, Germany, 2004
- 20) Gmehling, J. and U. Onken; Vapor-Liquid Equilibrium Data Collection, Esters: (Supplement 2), DECHEMA Chemistry Data Series, Vol.1, Part 5b, DECHEMA, Frankfurt/Main, Germany, 2002
- 21) Gmehling, J., U. Onken and P. Grenzheuser; Vapor-Liquid Equilibrium Data Collection, Carboxylic Acids, Anhydrides, Ethers, DECHEMA Chemistry Data Series, Vol. 1, Part 5, DECHEMA, Frankfurt/Main, Germany, 1982
- 22) Gmehling, J. and U. Onken; Vapor-Liquid Equilibrium Data Collection, Alcohols: Methanol (Supplement 5), DECHEMA Chemistry Data Series, Vol.1, Part 2g, DECHEMA, Frankfurt/Main, Germany, 2005
- 23) Gmehling, J., U. Onken and W. Arlt; Vapor-Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols (Supplement 1), DECHEMA Chemistry Data Series, Vol. 1, Part 2c, DECHEMA, Frankfurt/Main, Germany, 1982
- 24) Gmehling, J. and U. Onken; Vapor-Liquid Equilibrium Data Collection, Alcohols: Ethanol and 1,2-Ethandiol (Supplement 6), DECHEMA Chemistry Data Series, Vol.1, Part 2h, DECHEMA, Frankfurt/Main, Germany, 2006
- 25) Gmehling, J., U. Onken and U. Weidlich; Vapor-Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols and Phenols (Supplement 2), DECHEMA Chemistry Data Series, Vol.1, Part 2d, DECHEMA, Frankfurt/Main, Germany, 1982
- 26) Gmehling, J., U. Onken and W. Arlt; Vapor-Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols and Phenols, DECHEMA Chemistry Data Series, Vol.1, Part 2b, DECHEMA, Frankfurt/Main, Germany, 1978

(Received July 10, 2013)