Correlation of Infinite Dilution Activity Coefficients by Group-Contribution Methods
— Alkanol + Alkane Binary Systems —

Kenji FUKUCHI[a], Katsumi MIYOSHI[a], Toru WATANABE[b], and Yasuhiko ARAI[c]

[a] *Department of Chemical and Biological Engineering, Ube National College of Technology, Tokiwadai, Ube 755, Japan*
[b] *Department of Industrial Chemistry, Ariake National College of Technology, 150 Higashihagio, Omuta 870, Japan*
[c] *Department of Chemical Engineering, Kyushu University, 6–10–1 Hakozaki, Higashi–ku, Fukuoka 812–81, Japan*

Abstract

ASOG and UNIFAC which are two typical group-contribution methods were applied to calculate the infinite dilution activity coefficients of alkanol(methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, or 2-butanol) in alkane(hexadecane or tetradecane). The infinite dilution activity coefficients can be correlated by adjusting the ASOG group-interaction parameters between hydroxy(OH) and methyl(CH_2) groups.

Key Words : Phase Equilibrium, Activity Coefficient, Infinite Dilution, ASOG, UNIFAC, Alkanol, Alkane

1. Introduction

Infinite dilution activity coefficients are very important to predict the volatility of solute in a solvent and phase equilibria such as vapor-liquid and liquid-liquid equilibria. Therefore, the authors have measured the infinite dilution activity coefficients of alkanol in alkane by a gas stripping method[1].

In the present study, the experimental data reported were correlated by group-contribution methods, such as ASOG[2] and UNIFAC[3-5] which are often used in the process design. The interaction parameters between OH and CH_2 groups were reevaluated to give better correlation performance.

2. Group-Contribution Methods

2.1 ASOG

The infinite dilution activity coefficient γ_i^{∞} of a solute(alkanol) in a solvent(alkane) can be given by ASOG as follows[2].

$$\ln \gamma_i^{\infty} = \ln \gamma_i^{FH\infty} + \ln \gamma_i^{G\infty} \tag{1}$$

$$\ln \gamma_i^{FH\infty} = \ln \frac{\nu_i^{FH}}{\sum_j \nu_j^{FH} x_j} + 1 - \frac{\nu_i^{FH}}{\sum_j \nu_j^{FH} x_j} \tag{2}$$

[a] 宇部工業高等専門学校物質工学科
[b] 有明工業高等専門学校工業化学科
[c] 九州大学工学部化学機械工学科

$$\ln \gamma_i^G = \sum_k \nu_{ki}(\ln\Gamma_k - \Gamma_k^{(i)}) \tag{3}$$

$$\ln\Gamma_k = -\ln\sum_l X_l a_{kl} + 1 - \sum_l \frac{X_l a_{lk}}{\sum_m X_m a_{lm}} \tag{4}$$

where the group fraction for group k, X_k, is denoted as follows.

$$X_k = \sum_l X_l \nu_{kl} / \sum_l (X_l \sum_l \nu_{ll}) \tag{5}$$

The group Wilson parameter a_{kl} is empirically expressed as

$$\ln a_{kl} = m_{kl} + n_{kl}/T \tag{6}$$

2.2 UNIFAC

The values of γ_i^{∞} can also be derived from UNIFAC[3] as follows.

$$\ln\gamma_i^{\infty} = \ln\gamma_i^{C\infty} + \ln\gamma_i^{R\infty} \tag{7}$$

$$\ln \gamma_i^{C\infty} = \ln \frac{r_i}{r_2} + \frac{z}{2} q_i \ln\left(\frac{q_i r_2}{q_2 r_i}\right) + \frac{z}{2}(r_i - q_i) - (r_i - 1) - \frac{r_i}{r_2}\left\{\frac{z}{2}(r_2 - q_2) - (r_2 - 1)\right\} \tag{8}$$

where z is coordination number(z=10), r_i and q_i are volume parameter and surface parameter for component i. And they are given as follows.

$$r_i = \sum_k \nu_k^{(i)} R_k \tag{9}$$

$$q_i = \sum_k \nu_k^{(i)} Q_k \tag{10}$$

The residual part R of Eq. (7), due to energetic, is expressd as follows.

$$\ln \gamma_i^{R\infty} = \sum_k \nu_k^{(i)} (\ln\Gamma_k^{(2)} - \ln\Gamma_k^{(i)}) \tag{11}$$

where

$$\ln\Gamma_k = Q_k[1 - \ln(\sum_m \Theta_m \Psi_{mk}) - \sum_m \left(\frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}}\right)] \tag{12}$$

and the area fraction for group m, Θ_m, and the group-interaction parameter Ψ_{km} are given as

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \tag{13}$$

$$\Psi_{mn} = \exp\left(-\frac{a_{mn}}{T}\right) \text{ (Original and Bastos)} \quad \text{or} \quad \Psi_{mn} = \exp\left\{-\frac{(a_{mn} + b_{mn}T + c_{mn}T^2)}{T}\right\} \text{ (Weidlich)} \tag{14}$$

where X_m is the group fraction for group m in mixture and it is calculated in a similar manner to Eq. (5)(ASOG).

To calculate activity coefficients of i-th component from UNIFAC, group volume parameters R_k, group surface area parameters Q_k, group-interaction parameters a_{mn}, b_{mn}, and c_{mn} contained in Ψ_{mn} are needed. In the present study, three types of UNIFAC model were applied for infinite dilution activity coefficient. Their parameters are presented in Tables 1 - 4.

Table 1 UNIFAC group volume, surface area, and interaction parameters[3]

	CH_3	CH_2	CH	COH	MCOH	CHOH
R_k	0.9011	0.6744	0.4469	1.2044	1.4311	0.9769
Q_k	0.848	0.540	0.228	1.124	1.432	0.812

$a_{CH_2/COH}$ = 931.2 , a_{COH/CH_2} = 169.7

where COH:general case, MCOH:methanol, CHOH:secondary alkanol

Table 2 UNIFAC group volume, surface area, and interaction parameters[4]

	CH_3	CH_2	CH	OH	CH_3OH
R_k	0.9011	0.6744	0.4469	1.0000	1.4311
Q_k	0.848	0.540	0.228	1.200	1.432

$a_{CH_2/OH}$ = 1024.50 , a_{OH/CH_2} = 173.32

a_{CH_2/CH_3OH} = 917.16 , a_{CH_3OH/CH_2} = -34.51

Table 3 Modified UNIFAC group volume, surface area parameters[5]

	CH_3	CH_2	CH	OH(1-)	OH(2-)	OH(tert-)
R_k	0.6325	0.6325	0.6325	1.2302	1.0500	1.0500
Q_k	1.0608	0.7081	0.3554	0.8927	0.8789	0.7826

Table 4 Modified UNIFAC group interaction parameters[5]

m/n	a_{mn}	b_{mn}	c_{mn}
CH_2/OH	2777.0	-4.674	0.001551
OH/CH_2	1606.0	-4.746	0.0009181

where $\Psi_{mn} = \exp \{ - (a_{mn} + b_{mn}T + c_{mn}T^2) / T \}$

3. Prediction and Correlation

3.1 ASOG

The infinite dilution activity coefficients[1] were predicted by ASOG with the parameters reported in the literature. The interaction parameters(ASOG) between $-CH_2-$(alkane) and -OH (alkanol) are given as follows[2].

$$\ln a_{CH_2/OH} = -41.2503 + 7686.4 / T \quad (15)$$

$$\ln a_{OH/CH_2} = 4.7125 - 3060.0 / T \quad (16)$$

The prediction performance of ASOG is presented in Table 5 and a graphical illustration is given in Fig.1 for example. As shown in Table 5 and Fig.1, ASOG gives slightly larger values of the infinite dilution activity coefficients though the temperature dependency is correct.

To improve the correlation performance, we attempted to adjust the interaction parameters of ASOG. The two parameters, which are most effective, were adjusted here as Table 5(adjusted I and II) using the Marquardt method[6]. The correlation performance with adjusted parameters is presented in Table 5 and Figs. 1-9. As shown in the table and the figures, much improved results can be obtained.

3.2 UNIFAC

The prediction performance of UNIFAC are presented in Table 6 and a graphical illustration is given in Fig.1 for example. As shown in Table 6 and Fig.1, UNIFAC give smaller values of the infinite dilution activity coefficients in the original UNIFAC[3] and Weidlich modified UNIFAC[5], and the temperature dependency is not suitable in the original UNIFAC[3] and Bastos improved UNIFAC[4].

To improve the correlation performance using the original UNIFAC, we attempted to add a coefficient b_{mn} empirically to Ψ_{mn}, as shown in Table 6, which seems to be effective. Their values, $b_{CH_2/COH}$ and b_{COH/CH_2}, were determined by using the Marquardt method[6]. The correlation performances with modified parameters are presented in Table 6. As shown in the table, however, relatively large discrepancy still remains.

4. Conclusion

ASOG and UNIFAC which are two typical group-contribution methods were applied to calculate the infinite dilution activity coefficients of alkanol(methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, or 2-butanol) in alkane(hexadecane or tetradecane). The infinite dilution activity coefficients can be correlated by adjusting the ASOG group-interaction parameters between hydroxy(OH) and methyl(CH_2) groups. An improvement of UNIFAC should be considered in the future work.

Acknowledgement

The authors would like to acknowledge the financial support provided by the Grant-in-Aid for Scientific Research(C) of the Ministry of Education, Science, Sports and Culture, Japan(C-06650868, 1994 and C-07650909, 1995-1996).

Table 5 Prediction and correlation performance of infinite dilution activity coefficients of alkanol in hexadecane or tetradecane by ASOG

Solvent	Solute	ASOG original[2] Error[%]*	ASOG** adjusted(Ⅰ) Error[%]*	ASOG*** adjusted(Ⅱ) Error[%]*
Hexadecane	Methanol	14.2	37.9	27.4
	Ethanol	16.8	16.6	4.1
	1-Propanol	25.4	10.3	3.6
	2-Propanol	47.0	4.8	11.6
	1-Butanol	58.9	13.9	31.3
	2-Butanol	85.4	32.6	11.9
Tetradecane	Methanol	11.7	34.7	23.7
	Ethanol	14.5	18.3	5.6
	1-Propanol	20.3	14.1	2.9
	2-Propanol	41.1	1.3	15.1
	1-Butanol	40.4	5.2	16.1
	2-Butanol	77.8	26.8	6.9

$$*\text{Error}[\%]=\frac{100}{N}\Sigma\left|\gamma_{i,calc.}^{\infty}-\gamma_{i,exp.}^{\infty}\right|/\gamma_{i,exp.}^{\infty}\ ,\ N=\text{number of data}$$

** $m_{OH/CH2}$ = 4.3187 , $n_{OH/CH2}$ = -2822.1

*** 1-Alkanol $m_{OH/CH2}$ = 4.6742 , $n_{OH/CH2}$ = -2984.2

2-Alkanol $m_{OH/CH2}$ = 4.0319 , $n_{OH/CH2}$ = -2672.8

Table 6 Prediction and correlation performance of infinite dilution activity coefficients of alkanol in hexadecane or tetradecane by UNIFAC

Solvent	Solute	UNIFAC original[3] Error[%]*	UNIFAC Bastos[4] Error[%]*	UNIFAC Weidlich[5] Error[%]*	UNIFAC** adjusted(Ⅰ) Error[%]*	UNIFAC** adjusted(Ⅱ) Error[%]*
Hexadecane	Methanol	31.8	41.6	51.6	11.6	12.9
	Ethanol	50.4	27.4	27.8	27.5	32.4
	1-Propanol	47.2	27.2	18.8	26.0	27.0
	2-Propanol	78.2	23.6	24.2	60.0	31.3
	1-Butanol	34.7	28.3	6.8	43.4	29.8
	2-Butanol	70.2	31.2	3.8	41.3	26.6
Tetradecane	Methanol	37.1	39.2	49.0	10.9	12.7
	Ethanol	51.8	27.8	28.9	29.7	34.4
	1-Propanol	49.6	28.6	21.9	26.9	29.0
	2-Propanol	78.8	28.1	27.1	61.2	33.6
	1-Butanol	41.1	31.9	10.1	38.2	33.0
	2-Butanol	71.8	27.6	3.9	44.4	25.5

$$*\text{Error}[\%]=\frac{100}{N}\Sigma\left|\gamma_{i,calc.}^{\infty}-\gamma_{i,exp.}^{\infty}\right|/\gamma_{i,exp.}^{\infty}\ ,\ N=\text{number of data}$$

** $b_{CH2/OH}$ = -1.580 , $b_{OH/CH2}$ = 1.398 , where $\Psi_{mn}=\exp(b_{mn}-a_{mn}/T)$

*** 1-Alkanol $b_{CH2/OH}$ = -1.147 , $b_{OH/CH2}$ = 1.192

2-Alkanol $b_{CH2/OH}$ = -3.339 , $b_{OH/CH2}$ = 1.946

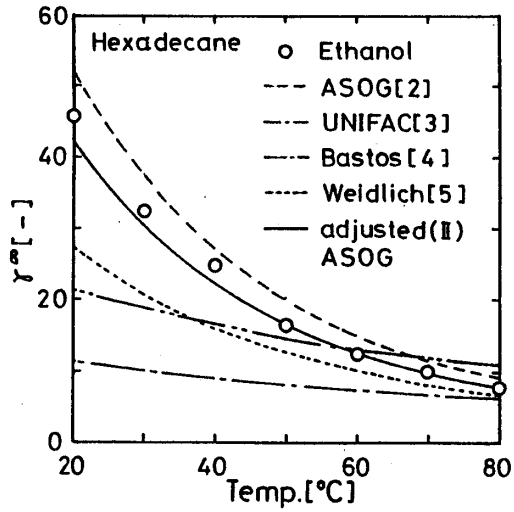

Fig.1 Prediction and Correlation performance of infinite dilution activity coefficients of ethanol in hexadecane by ASOG and UNIFAC

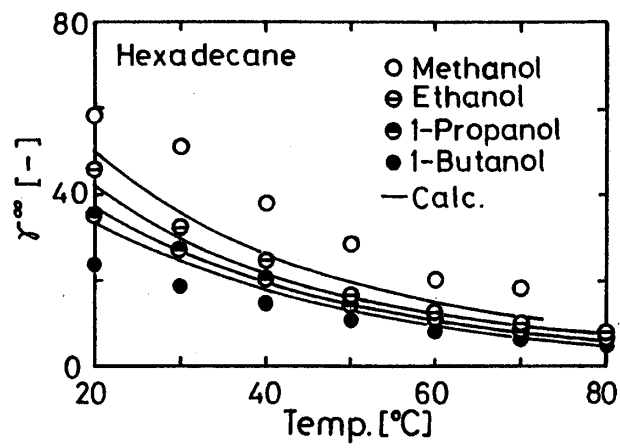

Fig.2 Correlation performance of infinite dilution activity coefficients of 1-alkanol in hexadecane by ASOG with adjusted parameters(adjusted (II) in Table 5)

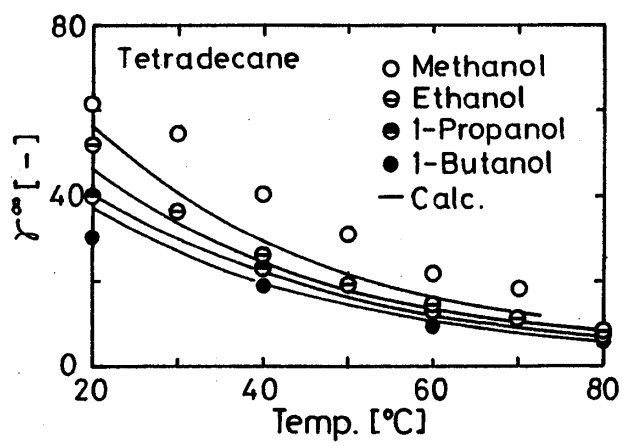

Fig.3 Correlation performance of infinite dilution activity coefficients of 1-alkanol in tetradecane by ASOG with adjusted parameters(adjusted (II) in Table 5)

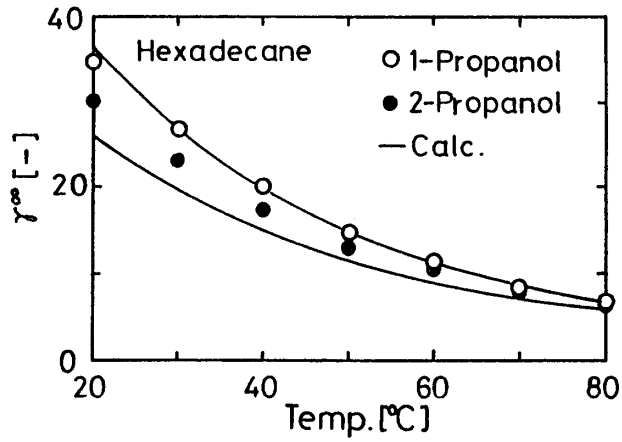

Fig.4 Correlation performance of infinite dilution activity coefficients of 1-propanol or 2-propanol in hexadecane by ASOG with adjusted parameters(adjusted (II) in Table 5)

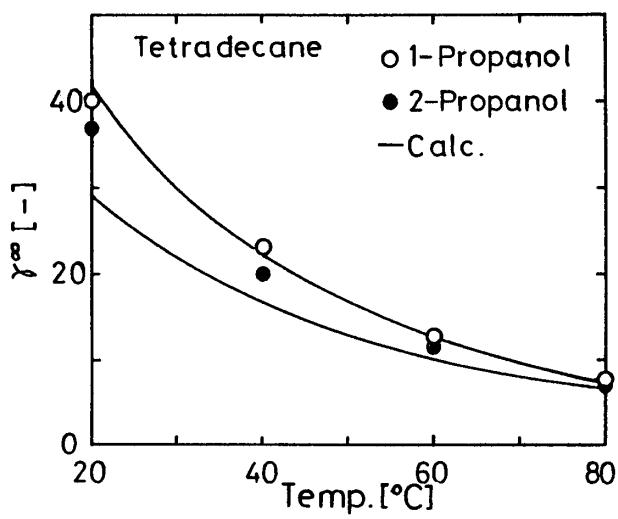

Fig.5 Correlation performance of infinite dilution activity coefficients of 1-propanol or 2-propanol in tetradecane by ASOG with adjusted parameters(adjusted (II) in Table 5)

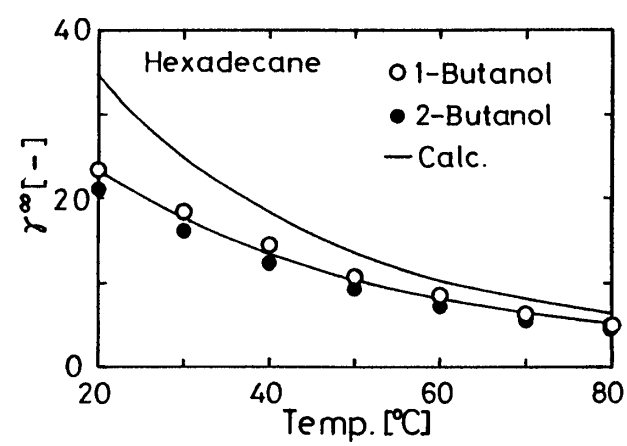

Fig.6 Correlation performance of infinite dilution activity coefficients of 1-butanol or 2-butanol in hexadecane by ASOG with adjusted parameters(adjusted (II) in Table 5)

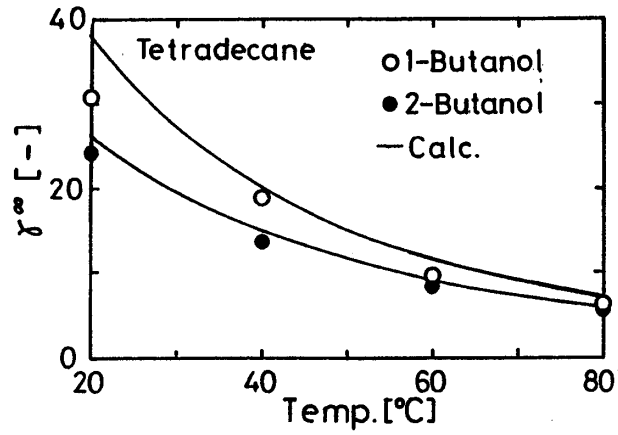

Fig.7 Correlation performance of infinite dilution activity coefficients of 1-butanol or 2-butanol in tetradecane by ASOG with adjusted parameters(adjusted (II) in Table 5)

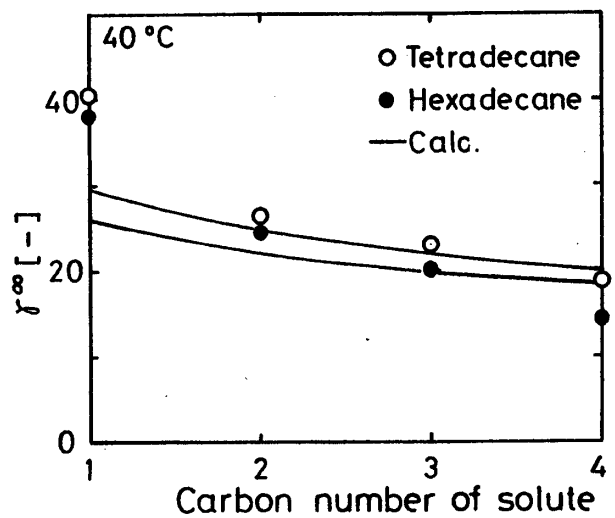

Fig.8 Correlation performance of infinite dilution activity coefficients of 1-alkanol in hexadecane or tetradecane by ASOG with adjusted parameters(adjusted (II) in Table 5)

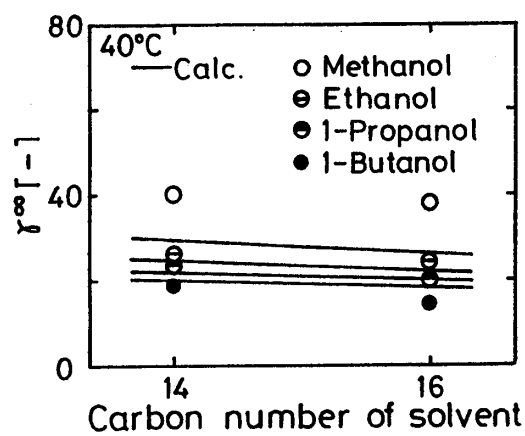

Fig.9 Correlation performance of infinite dilution activity coefficients of 1-alkanol in hexadecane or tetradecane by ASOG with adjusted parameters(adjusted (II) in Table 5)

Nomenclatures

a_{kl}	ASOG group Wilson parameter
a_{mn}	UNIFAC group interaction parameter
b_{mn}	UNIFAC group interaction parameter
c_{mn}	UNIFAC group interaction parameter
m_{kl}	ASOG group interaction parameters
n_{kl}	ASOG group interaction parameters
Q_k	surface parameter for group k
q_i	surface parameter for component i
R_k	volume parameter for group k
r_i	volume parameter for component i
T	temperature, K
t	temperature, ℃
X_k	group fraction for group k
x_i	mole fraction for component i
z	coordination number(z=10)

<Greek letters>

Γ_k	activity coefficient for group k
$\Gamma_k^{(i)}$	activity coefficient for group k in pure component i
γ	activity coefficient
Θ_m	area fraction for group m
ν_i	number of groups in molecule i
ν_i^{FH}	number of atoms(other than H) in molecule i
ν_{ki}	total number of atoms(other than H) in group k of molecule i
$\nu_k^{(i)}$	number of groups for group k in pure component i
Ψ_{nm}	group interaction parameter for UNIFAC

<Subscripts>

i, j	components i and j
k, l, m, n	groups k, l, m, and n
ki	group k in molecule i
1	solute(alkanol)
2	solvent(alkane)

<Superscripts>

C	combinatorial term
FH	size contribution(Flory-Huggins eqn.)
G	group contribution
(i)	standard state(pure component i)
R	residual term
∞	infinite dilution

References

[1] K. Fukuchi, K. Miyoshi, and Y. Arai, Kagaku Kogaku Ronbunshu, 22(1996)372-377.
[2] K. Tochigi, D. Tiegs, J. Gmehling, and K. Kojima, J. Chem. Eng. Japan, 23(1990)453-463.
[3] A. Fredenslund, , R. L. Jones, J. M. Prausnitz, AIChE J., 21(1975)1086-1099.
[4] J. C. Bastos, M. E. Soares, and A. G. Medina, Ind. Eng. Chem. Res., 27(1988)1269-1277.
[5] U. Weidlich and J. Gmehling, Ind. Eng. Chem. Res., 26(1987)1372-1381.
[6] D. W. Marquardt, J. Soc. Ind. Appl. Math., 11(1963)431-441.

Appendix

The infinite dilution activity coefficients of alkanol(methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, or 2-butanol) in alkane(hexadecane or tetradecane) already published [1] are summarized as appendix(Tables A-1 and A-2).

Table A-1 Infinite dilution activity coefficients of alkanol in hexadecane

Temp. [℃]	Methanol	Ethanol	1-Propanol	2-Propanol	1-Butanol	2-Butanol
20	58.0	45.8	34.9	30.2	23.5	21.2
30	51.2	32.4	27.0	23.1	18.5	16.1
40	38.2	24.4	20.1	17.3	14.5	12.3
50	28.5	16.6	14.7	13.1	10.8	9.47
60	20.0	12.6	11.3	10.5	8.52	7.47
70	18.2	10.1	8.35	8.16	6.50	6.05
80		8.03	6.83	6.60	5.15	5.04

Table A-2 Infinite dilution activity coefficients of alkanol in tetradecane

Temp. [℃]	Methanol	Ethanol	1-Propanol	2-Propanol	1-Butanol	2-Butanol
20	61.7	51.9	40.2	36.9	30.7	24.2
30	54.2	36.6				
40	40.5	26.5	23.1	20.0	18.9	13.6
50	31.2	19.6				
60	22.0	14.7	12.9	11.6	9.71	8.45
70	18.8	11.6				
80		8.86	7.92	7.36	6.31	6.05

(平成8年9月24日受理)