Prediction of Vapor-Liquid Equilibria and Solid-Liquid Equilibria by the Group Wilson Parameters Based on Total Vapor Pressure Data

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The Analytical Solutions of Groups model by use of the group Wilson parameters is one of the useful methods to predict liquid phase activity coefficients. The group Wilson parameters for the systems consisting of CH₂ groups and OH groups were determined using the total vapor pressure data of alcohol-water and alcohol-paraffin systems in the temperature range from 50°C to 90°C. The determined group Wilson parameters were successfully used for prediction of isobaric vapor-liquid equilibria with pressures up to 20 atm and temperatures up to 215°C.

Solid-liquid equilibria were also satisfactorily predicted at temperatures down to -81°C using the same parameters for predicting isobaric vapor-liquid equilibria.

1. Introduction

The knowledge of phase equilibrium data is essential for the design of distillation, crystallization and other industrial separation equipment. However, only a limited scope of suitable experimental data is usually available when new systems are considered. It is therefore necessary to interpolate or extrapolate the existing mixture data, or when no suitable data are available, to estimate the desired equilibrium data, resorting to some appropriate method which should be able to predict the properties of a wide ranges of mixtures from the experimental data on a limited number of reference systems. The Analytical Solutions of Groups (ASOG) model is one of the useful methods to serve the purpose.

Estimation of thermodynamic properties of liquid mixtures from group contributions was first suggested by Langmuir²²⁾. This suggestion, however, received little attention until Derr and Parado-poulos¹¹⁾, and Redlich, Derr and Pierotti³⁴⁾ used group contributions to correlate heats of mixing, followed by Wilson and Deal⁴⁵⁾ who developed the "Solution of Groups" model for estimating liquid phase activity coefficients. This model was expanded by Derr and Deal¹⁰⁾ into the ASOG model for the prediction of liquid phase activity coefficients in terms of the parameters associated with the pairs of structural groups of a solution.

The prediction of phase equilibria by the ASOG model has been shown by Ronc and Ratcliff³⁵⁾,

Tochigi and Kojima³⁹⁾, and authors¹⁷⁾ for vapor-liquid equilibria; by the authors¹⁷⁾ for solid-liquid equilibria; and by Tochigi and Kojima⁴⁰⁾ for liquid-liquid equilibria. In this paper, the method to determine the group Wilson parameters from the total vapor pressure data is shown.

Vapor-liquid equilibria and solid-liquid equilibria were also predicted by the parameters depending on isothermal vapor-liquid equilibrium data for comparing the predicted results from the parameters depending on the total vapor pressure data. The assumption of Maripuri and Ratcliff²³⁾ that aliphatic and aromatic carbon atoms can be treated as equivalent is used in this paper.

2. The Analytical Solutions of Groups Model

The Analytical Solutions of Groups (ASOG) model has been described in detail elsewhere^{10), 17), 35), 39)}. According to the ASOG model, the activity coefficient of a component *i* in a solution can be calculated from the following equations:

$$\ln \gamma_i = \ln \gamma_i^{FH} + \ln \gamma_i^G \quad (1)$$

$$\ln \gamma_i^{FH} = \ln U_i + (1 - U_i) \quad (2)$$

$$U_i = \frac{\nu_i^{FH}}{\sum_{j=1}^n \nu_j^{FH} x_j} \quad (3)$$

$$\ln \nu_i^G = \sum_k^N \nu_{ki} (\ln \Gamma_k - \ln \Gamma_k^*) \quad (4)$$

$$\ln \Gamma_k = -\ln \sum_l^N X_l a_{k/l} + \left[1 - \sum_l^N \frac{X_l a_{l/k}}{\sum_m^N X_m a_{l/m}} \right] \quad (5)$$

$$X_k = \frac{\sum_{i=1}^n x_i \nu_{ki}}{\sum_{i=1}^n x_i \sum_k^N \nu_{ki}} \quad (6)$$

where ν_i^{FH} is the number of atoms (other than hydrogen) in molecular species *i*. ν_{ki} is the number

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of interacting groups of kind k in molecule i . Γ_k is the group activity coefficient of group k and Γ_k^* is the group activity coefficient of group k at standard state. This standard state depends on molecule i . $a_{k/l}$, $a_{l/k}$ are group Wilson parameters and X is the group fraction.

3. Determination of the Group Wilson Parameters in the Analytical Solutions of Groups Model

For a solution containing only two groups 1 and 2, Eq. (4) is written as a function of a_{12} and a_{21} only at a given temperature as follows:

$$\ln \gamma_i^G = f_i(X_1, a_{12}, a_{21}) \quad (7)$$

The group Wilson parameters are determined by using the total vapor pressure data and isothermal vapor-liquid equilibrium data.

Defining

$$F = \left[\sum_{j=1}^m \sum_{i=1}^n (\ln \gamma_{i,\text{exp}}^G - \ln \gamma_{i,\text{cal}}^G) j^2 \right] \quad (8)$$

where j denotes the j^{th} experimental point, and F is a function of a_{12} and a_{21} . Seeking the best values of a_{12} and a_{21} by minimizing F , i. e., by solving for

$$\frac{\partial F}{\partial a_{12}} = \frac{\partial F}{\partial a_{21}} = 0 \quad (9)$$

Eq. (9) was solved by the damped least squares fit method^{17),35)}.

In this paper, the group Wilson parameters were obtained from the total vapor pressure data (P - t - x) but these data were taken equal to those of isothermal vapor-liquid equilibrium data (P - t - x - y) in the temperature range from 50°C to 90°C of the alcohol-water and alcohol-paraffin systems which were made up with CH_2 and OH groups. Also, using the same isothermal vapor-liquid equilibrium data (P - t - x - y), the group Wilson parameters were determined for the same systems in the same range of temperature. The equilibrium data used are shown in **Table 1**. For simplicity, no distinction is made between CH_3 and CH_2 groups. The water molecule is treated as 1.6^{17),36),39)} interaction OH

groups, and the value of CH_2 group in i -propanol is treated as 2.8^{17),39)}.

The following four methods are used to determine the group Wilson parameters:

(I) The method to determine the group Wilson parameters by using isothermal vapor-liquid equilibrium data

(I-a) Calculate γ_i in Eq. (1) by the following Eq. (10).

$$\gamma_i = \frac{y_i P}{x_i P_i^s} \quad (10)$$

(I-b) Calculate γ_i in Eq. (1) by the following Eq. (11)

$$\gamma_i = \frac{P \phi_i^v y_i}{x_i f_i^{\circ L}} \quad (11)$$

where ϕ_i^v is the vapor phase fugacity coefficient of component i , and $f_i^{\circ L}$ is the fugacity of pure component i in the liquid phase. $f_i^{\circ L}$ is given by

$$f_i^{\circ L} = P_i^s \phi_i^s \exp[V_i^L(P - P_i^s)/RT] \quad (12)$$

where ϕ_i^s is the fugacity coefficient of pure vapor i at temperature T and saturation pressure P_i^s , and V_i^L is the liquid molar volume of pure component i . P^s is calculated by the Antoine equation using constants of Dean⁹⁾ and Boublík, et al.⁵⁾. Moreover, using the liquid molar volumes at three different temperatures^{16),38)}, the constants in the quadratic equations

$$V^L = A + BT + CT^2 \quad (13)$$

were calculated for each component³²⁾. The liquid molar volumes at any temperature could then be calculated when required in the computer program by using Eq. (13). ϕ_i^v and ϕ_i^s are estimated from the correlation of Nagahama and Hirata²⁶⁾.

(II) The method to determine the group Wilson parameters by using the total vapor pressure data

For an n -component mixture, the activity coefficient is represented by the Wilson equation⁴⁴⁾ as follows:

$$\ln \gamma_i = -\ln \left[\sum_{j=1}^n x_j A_{ij} \right] + \left[1 - \sum_{k=1}^n \frac{x_k A_{ki}}{\sum_{j=1}^n x_j A_{kj}} \right] \quad (14)$$

where,

$$A_{ij} \equiv \frac{V_j^L}{V_i^L} \exp \left[-\frac{(\lambda_{ij} - \lambda_{ii})}{RT} \right] \quad (15)$$

The total vapor pressure of an n -component mixture can be calculated by Eq. (16) or Eq. (17).

$$P = \sum_{i=1}^n \gamma_i P_i^s x_i \quad (16)$$

$$P = \sum_{i=1}^n \gamma_i f_i^{\circ L} x_i / \phi_i^v \quad (17)$$

Usually, the total vapor pressure method is used to calculate the equilibrium vapor composition (y_i)

Table 1 Phase Equilibrium Data Used for the Determination of the Group Wilson Parameters

Temp. (°C)	System
50	Methanol-Water ²⁴⁾ , Ethanol-Water ¹²⁾ Ethanol- n -Heptane ³⁷⁾
60	Methanol-Water ⁶⁾ , Ethanol-Water ⁴¹⁾ n -Propanol-Water ²⁵⁾ , i -Propanol- n -Heptane ⁴²⁾
90	n -Propanol-Water ³³⁾ , n -Propanol- n -Decane ³³⁾

from experimental T and x_i . And the method of calculation used in this paper is as follows:

Defining

$$F = \sum_{i=1}^n \left(\frac{P_{exp} - P_{cal}}{P_{exp}} \times 100 \right)_i^2 \tag{18}$$

where, P_{exp} is the experimental total vapor pressure and P_{cal} is calculated by Eq. (16) or Eq. (17) using experimental T and x_i .

Namely, to calculate γ_i of Eq. (14), a suitable parameter ($\lambda_{ij}-\lambda_{ii}$) can be determined by pattern search method so that F is minimized. From these results, the equilibrium vapor compositions are calculated from Eq. (19) or Eq. (20).

$$y_i = \frac{\gamma_i P_i^s x_i}{P_{cal}} \tag{19}$$

$$y_i = \frac{\gamma_i f_j^{\circ L} x_i}{\phi_i^v P_{cal}} \tag{20}$$

(II-a) Calculate γ_i in Eq. (1) by the above method using Eq. (16)

(II-b) Calculate γ_i in Eq. (1) by the above method using Eq. (17)

The group Wilson parameters determined at 50, 60 and 90°C were listed in **Table 2** and they were satisfactorily correlated with functions of absolute temperature as follows:

(I-a)
$$a_{CH_2/OH} = \exp \left(-1.6952 + \frac{158.3}{T} \right) \tag{21}$$

$$a_{OH/CH_2} = \exp \left(1.4812 - \frac{1803.0}{T} \right) \tag{22}$$

Table 2 Determined Group Wilson Parameters

Temp. (°C)	$a_{CH_2/OH}$	a_{OH/CH_2}	R. M. S. D.
(I-a)			
50	0.3005	0.0169	0.0890
60	0.2935	0.0190	0.1121
90	0.2840	0.0309	0.0491
(I-b)			
50	0.2954	0.0179	0.0869
60	0.2925	0.0185	0.0848
90	0.2863	0.0348	0.0471
(II-a)			
50	0.2955	0.0128	0.0617
60	0.2830	0.0188	0.0738
90	0.2886	0.0379	0.0318
(II-b)			
50	0.2906	0.0144	0.0463
60	0.2828	0.0198	0.0606
90	0.2951	0.0368	0.0262

$$R. M. S. D. = \sqrt{\left[\sum_{j=1}^m \sum_{i=1}^n (\ln \gamma_{i,exp}^a - \ln \gamma_{i,cal}^a) j^2 \right] / m}$$

(I-b)
$$a_{CH_2/OH} = \exp \left(-1.4973 + \frac{90.3}{T} \right) \tag{23}$$

$$a_{OH/CH_2} = \exp \left(2.3102 - \frac{2066.0}{T} \right) \tag{24}$$

(II-a)
$$a_{CH_2/OH} = \exp \left(-1.3529 + \frac{38.6}{T} \right) \tag{25}$$

$$a_{OH/CH_2} = \exp \left(5.2781 - \frac{3099.2}{T} \right) \tag{26}$$

(II-b)
$$a_{CH_2/OH} = \exp \left(-1.0267 - \frac{71.0}{T} \right) \tag{27}$$

Table 3 Deviations of Predicted Data from Experimental Vapor-Liquid Equilibrium Data for Binary Systems

System Component (1) -Component (2)	Press. (mmHg)	Temp. Range (°C)	Δy_1^*				Δt^*				n^*	Ref.	Note
			(I-a)	(I-b)	(II-a)	(II-b)	(I-a)	(I-b)	(II-a)	(II-b)			
Methanol-Water	760	64.65—100.0	4	8	4	9	0.3	0.6	0.3	0.6	15	8)	
Ethanol-Water	760	78.15—100.0	7	8	7	8	0.36	0.34	0.35	0.35	15	7)	
n-Propanol-Water	760	87.7 —100.0	22.7	24.3	23.8	26.7	0.80	0.66	0.87	0.76	19	20)	
Methanol-Ethanol	760	64.65— 78.3	8	6	8	6	0.3	0.3	0.3	0.3	12	1)	
Methanol-i-Propanol	760	64.65— 82.4	15	12	15	12	0.9	0.8	0.9	0.8	8	3)	
Ethanol-i-Propanol	760	78.3 — 82.4	2.4	2.6	2.4	2.6	0.1	0.1	0.1	0.1	13	3)	
Ethanol-n-Butanol	760	78.3 —117.5	12	7	12	7	0.2	0.4	0.2	0.5	9	14)	
i-Propanol-n-Propanol	760	82.4 — 97.2	5.3	6.1	5.3	6.1	0.2	0.2	0.2	0.2	14	3)	
Methanol-n-Heptane	760	58.81— 98.42	8	5	9	6	0.49	0.21	0.30	0.19	7	4)	
Ethanol-n-Hexane	760	58.4 — 78.32	15	17	15	16	1.23	0.88	1.08	0.75	9	21)	
Ethanol-n-Heptane	760	71.0 — 98.4	35	42	40	43	2.1	1.9	2.4	2.0	18	18)	
n-Propanol-n-Hexane	760	65.7 — 97.2	42.5	44.9	43.4	45.3	1.5	1.6	1.6	1.6	12	29)	
n-Propanol-n-Heptane	760	84.6 — 98.4	17	16	16	16	0.9	0.5	1.3	0.6	9	13)	
n-Butanol-n-Octane	760	108.5 —125.7	16	18	32	26	0.9	0.9	2.1	1.5	10	19)	
n-Butanol-n-Nonane	760	115.9 —150.8	8	7	19	12	0.5	0.7	1.8	1.3	9	19)	
Ethanol-Benzene	760	67.9 — 80.1	31	29	31	30	2.5	2.7	2.5	2.8	10	27)	
n-Propanol-Benzene	760	76.0 — 97.2	54	49	50	48	1.7	1.9	1.5	1.8	12	29)	
n-Butanol-n-Heptane	1,445	114.8 —137.0	26	31	40	37	1.2	1.2	3.0	2.1	10	43)	
Methanol-Water	3,800	112.2 —152.3	12.8	7.5	11.1	10.2	1.0	1.5	1.1	1.8	22	15)	5 atm
Methanol-Water	6,080	129.1 —169.5	14.9	5.8	12.6	8.6	0.7	1.3	1.0	1.6	22	15)	8 atm
Methanol-Water	8,512	142.0 —185.4	17.7	4.7	15.2	8.0	0.5	1.3	0.9	1.8	22	15)	11.2atm
Ethanol-Water	2,586	112.6 —135.6	17	10.1	13	5	0.6	0.5	0.4	0.2	18	28)	50 psia
Ethanol-Water	5,172	136.7 —164.2	31	18	23	9	2.2	1.9	1.6	1.2	18	28)	100 psia
Ethanol-Water	10,344	164.2 —194.1	43	27	32	15	3.6	3.5	2.5	2.2	18	28)	200 psia
Ethanol-Water	15,512	182.6 —213.8	59	39	42	21	5.0	4.8	3.3	3.0	11	28)	300 psia

* $\Delta y_1^* = [\sum |(y_{1,exp} - y_{1,cal})|] / n \times 1,000$ * $\Delta t^* = [\sum |(t_{exp} - t_{cal})|] / n$, * n =No. of data points

$$a_{\text{OH/CH}_2} = \exp\left(4.1176 - \frac{2690.3}{T}\right) \quad (28)$$

4. Prediction of Vapor-Liquid Equilibria

The liquid phase activity coefficients of component i of vapor-liquid equilibria were calculated from Eq.(10) or Eq.(11). They can be written for the equilibrium vapor composition of component i as follows:

$$\sum_{i=1}^n y_i = \sum_{i=1}^n \gamma_i P_i^s x_i / P = 1 \quad (29)$$

$$\sum_{i=1}^n y_i = \sum_{i=1}^n \gamma_i f_i^{\circ L} x_i / \phi_i^v P = 1 \quad (30)$$

The activity coefficients in Eq.(29) are predicted by using Eqs.(1) to (6) with parameters (I-a) and (II-a), and the activity coefficients in Eq.(30) are predicted by using also Eqs.(1) to (6) but with parameters (I-b) and (II-b).

The predicted results for the 25 isobaric vapor-liquid equilibria of alcohol-water, alcohol-alcohol, alcohol-paraffin and alcohol-aromatic hydrocarbon systems are shown in **Table 3** with the absolute arithmetic mean deviations between experimental and predicted vapor compositions and temperature data. The benzene molecule is treated as 6.0 interaction CH_2 group.

Figs. 1 and 2 show the predicted vapor-liquid equilibria with respect to parameter (II-b) to the deviation of experimental temperature with the composition data for ethanol- n -butanol and ethanol-water systems, respectively.

The predicted results in **Table 3** and **Figs. 1** and **2** show good agreement with those of the experi-

Fig. 1 Temperature-Composition Diagram for Ethanol (1)- n -Butanol (2) System at 760 mmHg

Fig. 2 Temperature-Composition Diagram for Ethanol (1)-Water (2) System at 2,586 mmHg

ments.

5. Prediction of Solid-Liquid Equilibria

The liquid phase activity coefficients for the solute component i of solid-liquid equilibria in which the solid phase is assumed to be the pure solute and the liquid phase is a saturated solution of the solute in the solvent can be determined by the simple Van't Hoff isochore equation, i.e.

$$\ln \gamma_i x_i = \frac{\Delta H_i}{RT} - \frac{(T - T_i^M)}{T_i^M} \quad (31)$$

where ΔH_i is the heat of fusion of the solute component i and T_i^M is the temperature of melting point of the solute component i .

The activity coefficients in Eq.(31) are predicted by using Eqs.(1) to (6).

The predicted results for solid-liquid equilibria of naphthalene-alcohol and benzene-alcohol systems are listed in **Table 4** with the absolute arithmetic mean deviations between experimental and predicted liquid compositions. **Figs. 3 and 4** show the predicted solid-liquid equilibria with respect to parameter (II-b) to the deviation of experimental temperature with the liquid composition data for naphthalene- i -butanol and benzene- i -propanol systems. Assuming the systems ideal, i.e. γ_i in Eq.(31) is taken to be 1.0, the calculated results are also plotted in **Figs. 3 and 4**.

The predicted solid-liquid equilibrium data shown in **Table 4** and **Figs. 3 and 4** indicated good agree-

Table 4 Deviations of Predicted Data from Experimental Solid-Liquid Equilibrium Data for Binary Systems

System Component (1)-Component (2)	Δx_1^*				Temp. Range (°C)	n *	Ref.
	(I-a)	(I-b)	(II-a)	(II-b)			
Naphthalene-Ethanol	55.1	49.9	57.2	53.2	20.0-80.0	11	2)
Naphthalene- <i>n</i> -Propanol	38.6	34.8	42.4	38.5	20.0-80.0	11	2)
Naphthalene- <i>i</i> -Propanol	45.9	41.0	48.6	44.9	20.0-80.0	11	2)
Naphthalene- <i>n</i> -Butanol	32.2	28.8	37.6	33.1	25.0-80.0	10	2)
Naphthalene- <i>i</i> -Butanol	30.4	26.9	31.6	28.2	20.0-80.0	11	2)
Benzene- <i>n</i> -Propanol	27.3	32.8	69.6	54.6	-78.6- 5.5	8	31)
Benzene- <i>i</i> -Propanol	30.6	37.0	58.0	52.4	-79.0- 5.5	12	30)
Benzene- <i>n</i> -Butanol	39.4	40.9	49.2	45.9	-81.0- 5.5	12	30)

* $\Delta x_1^* = [\sum |(x_{1,exp} - x_{1,cal})| / N] \times 1,000$ * n = No. of data points

Fig. 3 Solubility Diagram of Solid Naphthalene in Liquid Phase for Naphthalene (1)-*i*-Butanol (2) System

Fig. 4 Solubility Diagram of Solid Benzene in Liquid Phase for Benzene (1)-*i*-Propanol (2) System

ment with those of the experiments.

The naphthalene molecule is treated as 10.0 interaction CH_2 groups and the value of CH_2 group in *i*-butanol is taken as 3.8, which was of the same treatment as Tochigi and Kojima³⁹⁾ and the authors¹⁷⁾. ΔH for naphthalene is taken from Timmermans³⁸⁾ and ΔH for benzene is taken from Dean⁹⁾.

6. Conclusions

The group Wilson parameters for the systems

consisting of CH_2 and OH groups were determined using the total vapor pressure data of alcohol-water and alcohol-paraffin systems at temperatures 50, 60 and 90°C. The isobaric vapor-liquid equilibria of the binary systems involving alcohols, water, paraffins and benzene were satisfactorily predicted even within the temperature range from 90°C to 215°C and pressures up to 20 atm. Also, solid-liquid equilibria of the naphthalene-alcohol and benzene-alcohol systems were successfully predicted at temperatures down to -81°C utilizing the same parameters for predicting isobaric vapor-liquid equilibria.

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Nomenclature

A, B, C	= Antoine constant	[—]
a	= group Wilson parameter	[—]
$f_i^{\circ L}$	= fugacity of pure component i in the liquid phase	[mmHg]
ΔH	= heat of fusion	[cal/g-mol]
m	= number of data points used to determine the parameters	[—]
N	= number of groups	[—]
n	= number of components	[—]
P	= total vapor pressure	[mmHg]
P^s	= vapor pressure of pure liquid component	[mmHg]
R	= gas constant	[cal/g-mol·K]
T	= absolute temperature	[K]
U	= solute group ratio	[—]
V^L	= liquid molar volume	[cc/g-mol]
X	= group fraction	[—]
x	= mole fraction in liquid phase	[—]
y	= mole fraction in vapor phase	[—]
Γ	= group activity coefficient	[—]
γ	= activity coefficient	[—]
$\lambda_{ij} - \lambda_{ii}$	= Wilson parameter	[cal/g-mol]
ν_i^{FH}	= number of atoms (other than hydrogen) in molecular species i	[—]

- ν_{ki} =number of interacting groups of
kind k in molecule i [—]
 ϕ^v =vapor phase fugacity coefficient [—]
 ϕ^s =pure vapor fugacity coefficient [—]

Subscripts

- 1, 2, i , j =molecule 1, 2, i and j
 k , l , m =group k , l and m
 ki =group k in molecule i
 cal =calculated

Superscripts

- FH =size contribution
 G =group contribution
 L =liquid phase
 M =melting point
 S =pure component
 V =vapor phase

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要 旨

全圧データに基づくグループ Wilson パラメータを用いた気液平衡および固液平衡の推算

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グループ Wilson パラメータを用いる解析的グループ溶液モデル (ASOG モデル) は、液相活量係数を推算する有用な方法の一つである¹⁰⁾。すでに、ASOG モデルによる相平衡の推算として、気液平衡については、Ronc および Ratcliff³⁵⁾、栃木および小島³⁹⁾、筆者ら¹⁷⁾の研究が、固液平衡については筆者ら¹⁷⁾の研究が、さらに液液平衡については栃木および小島⁴⁰⁾の研究がある。

グループ溶液モデルにおける混合物中の成分 i の活量係数 γ_i は、Eqs. (1)~(6) で表わされる。Eq. (5) 中の $a_{l/k}$, $a_{l/k}$ がグループ Wilson パラメータである。

本研究では、 CH_2 と OH から成る系の検討を目的とし、(8) 式で示した目的関数 F が最小となるような、グループ Wilson パラメータを修正 Newton 法^{17), 35)}によって求めた。Table 1 に、パラメータ決定に用いた 50°C から 90°C の CH_2 と OH から成るアルコール-水、アルコール-パラフィン系の定温気液平衡データ (P - T - x - y) を示した。また、Table 1 に示した定温気液平衡データ (P - T - x - y) の y を除いた (P - T - x) を全圧データとして用いた。

パラメータの決定に次の四つの方法を用いた。

(I) 定温気液平衡データを用いる方法

(I-a) Eq.(1)中の γ_i を Eq.(10) で求めて、グループ Wilson

パラメータを求める方法

(I-b) Eq.(1)中の γ_i を Eq.(11) で求めて、グループ Wilson パラメータを求める方法

(II) 全圧データを用いる方法

(II-a) Eq. (16) を用いて全圧を計算し、その時計算される γ_i を Eq. (1) に用いて、グループ Wilson パラメータを求める方法

(II-b) Eq. (17) を用いて全圧を計算し、その時計算される γ_i を Eq. (1) に用いて、グループ Wilson パラメータを求める方法

以上の四つの方法によって決定した、グループ Wilson パラメータを Table 2 に示した。また、それらのパラメータを、Eqs. (21)~(28) で相関した。決定したグループ Wilson パラメータ [Eqs. (21)~(28)] を用いて、温度 $58\sim 214^\circ\text{C}$ 、圧力 $1\sim 20\text{ atm}$ までの定圧気液平衡の推算を行い、実測値と比較しその結果を Table 3 と Figs. 1, 2 に示したところ、推算値は実測値と良好な一致を示した。同様に、 $80\sim 81^\circ\text{C}$ の温度範囲の固液平衡の推算を行い、実測値と比較しその結果を Table 4 と Figs. 3, 4 に示したところ、推算値は実測値と良好な一致を示した。

本研究では、 CH_3 グループは CH_2 グループとして扱い、ベンゼン および ナフタレン はそれぞれ CH_2 6 グループおよび CH_2 10 グループより成るものとした²³⁾。また、 i -プロパノールおよび i -ブタノールの CH_2 グループ数は、それぞれ 2.8 および 3.8 とした^{17), 39)}。さらに、水は OH 1.6 グループより成るものとして扱った^{17), 36), 39)}。

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Keyword

Equilibria, Group Wilson parameter, Prediction, Solid-liquid, Vapor-liquid