Prediction of Vapor-Liquid Equilibria and Solid-Liquid Equilibria by the Analytical Solutions of Groups Model*

by Daisuke Hoshino**, Yoshiki Unno**, Kunio Nagahama**
and Mitsuho Hirata**

Summary: The group Wilson parameters to predict liquid phase activity coefficients by the Analytical Solutions of Groups model for the systems consisting of CH_2 groups and OH groups were determined using isothermal vapor-liquid equilibrium data of the alcohol-water and alcohol-paraffin systems in the temperature range 30°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 . And, isobaric vapor-liquid equilibria were also predicted by the parameters of Tochigi and Kojima, and Derr and Deal, respectively, for comparing the predicted results with those of our work.

Also, solid-liquid equilibria were well predicted by the extended use of the Analytical Solutions of Groups model utilizing the same parameters for predicting isobaric vapor-liquid equilibria.

1 Introduction

Phase equilibrium data are very important and useful for designing separation processes, for example, vapor-liquid equilibrium data for distillation and solid-liquid equilibrium data for crystallization. However only limited experimental data are available for any particular conditions of temperature, pressure and composition that are required for particular design. The "Analytical Solutions of Groups" (ASOG) model is one of the useful methods to interpolate or extrapolate the existing mixture data, or when the suitable data are not available, to estimate the desired equilibrium data.

A method for estimating liquid phase activity coefficients from group contributions was discussed and illustrated by Wilson and Deal³¹⁾ as the "Solution of Groups" model. The ASOG model discussed by Derr and Deal⁸⁾, Tochigi and Kojima²⁷⁾, and Ronc and Ratcliff²⁸⁾ were based on the "Solution of Groups" model. By the ASOG model, liquid phase activity coefficients were predicted in terms of the parameters associated with the pairs of structural groups of the solution.

The prediction of vapor-liquid equilibria by the ASOG model has already been shown by Derr and Deal, Tochigi and Kojima, and Ronc and Ratcliff. This paper deals not only with the

prediction of vapor-liquid equilibria, but the application of the ASOG model to the prediction of solid-liquid equilibria which has not been discussed in the literature. And the assumption of Maripuri and Ratcliff¹⁹⁾ is used in this paper that aliphatic and aromatic carbon atoms can be treated as equivalent.

2 The Analytical Solutions of Groups Model

In the Analytical Solutions of Groups model, the activity coefficient of a component i in solution is expressed as the sum of two contributions—one associated with the difference in molecular sizes and the other with the interaction of structural groups, as follows:

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

where $\ln \gamma_i^{\text{FH}}$ is the size contribution and $\ln \gamma_i^{\text{g}}$ is associated with the interaction of the structural groups of the molecule with those of its environment.

The size term is treated in the Flory-Huggins-like manner as Eqs. (2) and (3).

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

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

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

The interaction term is treated as the difference between the group contributions which arise in the solution and in the molecular standard states; these contributions are summed over all interaction groups comprising the solute molecules of interest.

* Received Jan. 18, 1977.

** Department of Industrial Chemistry, Faculty of Engineering, Tokyo Metropolitan University (1-1, Fukazawa, 2-chome, Setagaya-ku, Tokyo 158)

Thus:

$$\ln \gamma_i^G = \sum_k \nu_{ki} (\ln \Gamma_k - \ln \Gamma_i^L) \quad (4)$$

where ν_{ki} is the number of interacting groups of kind k in molecule i . Γ_k is the group activity coefficient of group k and is calculated by the Wilson equation.

The form of the Wilson equation in representing group activity coefficient is given in Eq. (5). For a group, k , in a mixture making up N groups:

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

where $a_{k/l}$, $a_{l/k}$ are group Wilson parameters and X are group fractions. The group fraction for group k is defined as the ratio of the total number of groups, k , from all sources to the total number of groups of all kinds in the mixture.

For a group k :

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

where x is the mole fraction, and the sums are to be taken over all groups, k , and components, i , in the solution.

3 Determination of Parameters in the Analytical Solutions of Groups Model

For the case of a solution containing only two groups 1 and 2, Eq. (5) becomes:

$$\ln \Gamma_1 = -\ln(X_1 + a_{12}X_2) + X_2 \left[\frac{a_{12}}{X_1 + a_{12}X_2} - \frac{a_{21}}{a_{21}X_1 + X_2} \right] \quad (7)$$

$$\ln \Gamma_2 = -\ln(a_{21}X_1 + X_2) - X_1 \left[\frac{a_{12}}{X_1 + a_{12}X_2} - \frac{a_{21}}{a_{21}X_1 + X_2} \right] \quad (8)$$

Using Eqs. (7) and (8), Eq. (4) is written as a function of a_{12} and a_{21} only at a given temperature as follows:

$$\ln \gamma_i^G = f_i(X_1, a_{12}, a_{21}) \quad (9)$$

The group Wilson parameters are determined by using isothermal vapor-liquid equilibrium data.

Defining

$$F = \left[\sum_{j=1}^m \sum_{i=1}^n (\ln \gamma_{i,exp}^G - \ln \gamma_{i,calc}^G)^2 \right] \quad (10)$$

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

$$\frac{\partial F}{\partial a_{12}} = \frac{\partial F}{\partial a_{21}} = 0 \quad (11)$$

Direct solution of Eq. (11) appeared difficult, and a computer program was written in which the group Wilson parameters were obtained by the damped least squares fit method. The form of Eq. (5) is such that negative parameters may give rise to logarithms of negative numbers. Consequently, only positive parameters have been considered meaningful. When the parameter became negative, calculation was stopped and new calculation was made again from the initial calculation of the program using the new initial values of a_{12} and a_{21} to minimize F .

In this paper, the group Wilson parameters were obtained by isothermal vapor-liquid equilibrium data in the temperature range from 30°C to 90°C of the alcohol-water and alcohol-paraffin systems which were made up with CH_2 and OH groups. For simplicity, no distinction is made between CH_3 and CH_2 groups. The equilibrium data used are shown in **Table 1**. The water molecule is treated as 1.6 interaction OH groups, and the value of CH_2 group in i -propanol is treated as 2.8, which were the same treatments used by Tochigi and Kojima.

The group Wilson parameters determined at 30, 50, 60 and 90°C are listed in **Table 2** and they were satisfactorily correlated with a function of absolute temperature as follows:

$$a_{\text{CH}_2/\text{OH}} = \exp \left(-0.9323 - \frac{105.9}{T} \right) \quad (12)$$

$$a_{\text{OH}/\text{CH}_2} = \exp \left(1.1373 - \frac{1684.8}{T} \right) \quad (13)$$

Eqs. (12) and (13) were successfully used even within the temperature range from 90°C to 215°C

Table 1 Isothermal Vapor-Liquid Equilibrium Data Used for the Determination of the Group Wilson Parameters

Temp. (°C)	System
30	<i>n</i> -Propanol-Water ³²⁾ , Ethanol- <i>n</i> -Hexane ¹³⁾
50	Methanol-Water ¹⁹⁾ , Ethanol-Water ⁹⁾ , Ethanol- <i>n</i> -Heptane ²⁶⁾
60	Methanol-Water ⁵⁾ , Ethanol-Water ²⁸⁾ , <i>n</i> -Propanol-Water ²⁰⁾ , <i>i</i> -Propanol- <i>n</i> -Heptane ²⁹⁾
90	<i>n</i> -Propanol-Water ²⁴⁾ , <i>n</i> -Propanol- <i>n</i> -Decane ²⁴⁾

that will be shown later in the part of the prediction of the isobaric vapor-liquid equilibria.

Table 2 Determined Group Wilson Parameters

Temp. (°C)	$a_{CH_2/OH}$	a_{OH/CH_2}	R.M.S.D.
30	0.2648	0.0123	0.0914
50	0.3005	0.0169	0.0890
60	0.2935	0.0190	0.1121
90	0.2840	0.0309	0.0491

$$R.M.S.D. = \sqrt{\left[\sum_{j=1}^m \sum_{i=1}^n (\ln \gamma_{i,exp}^0 - \ln \gamma_{i,cal}^0)^2 \right] / m}$$

4 Prediction of Vapor-Liquid Equilibria

The liquid phase activity coefficients for the component i of vapor-liquid equilibria were calculated from the following relationship,

$$\gamma_i = \frac{y_i \pi}{x_i P_i^0} \quad (14)$$

Eq. (14) can be written for the vapor composition of the component i , as follows:

$$\sum_{i=1}^n y_i = \sum_{i=1}^n \gamma_i P_i^0 x_i / \pi = 1 \quad (15)$$

The activity coefficients in Eq. (15) are predicted by using Eqs. (1) to (6).

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 ex-

perimental and predicted vapor compositions and temperature data. The deviations obtained from the parameters of Derr and Deal, and Tochigi and Kojima are also shown in **Table 3**. The benzene molecule is treated as 6.0 interaction CH_2

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

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)	Absolute Arithmetic Deviation						N*	Ref.	Note
			$y_1 \times 1,000$			$t [^\circ\text{C}]$					
			This Work	T.K*	D.D*	This Work	T.K*	D.D*			
Methanol–Water	760	64.65–100.0	5	6	13	0.4	0.4	1.0	15	7)	
Ethanol–Water	760	78.15–100.0	7	7	24	0.35	0.39	1.4	15	6)	
<i>n</i> –Propanol–Water	760	87.7 –100.0	25.7	26.4	50	1.11	1.14	2.32	19	16)	
Methanol–Ethanol	760	64.65– 78.3	15	15	15	0.3	0.3	0.3	12	1)	
Methanol– <i>i</i> –Propanol	760	64.65– 82.4	15	15	—	0.9	0.9	—	8	3)	
Ethanol– <i>i</i> –Propanol	760	78.3 – 82.4	40.3	40.3	—	0.1	0.1	—	13	3)	
Ethanol– <i>n</i> –Butanol	760	78.3 –117.5	12	12	12	0.2	0.2	0.2	9	11)	
<i>i</i> –Propanol– <i>n</i> –Propanol	760	82.4 – 97.2	5.3	5.3	—	0.2	0.2	—	14	3)	
Methanol– <i>n</i> –Heptane	760	58.81– 98.42	9	8	9	0.48	0.51	0.19	7	4)	
Ethanol– <i>n</i> –Hexane	760	58.4 – 78.32	15	16	14	1.24	1.26	0.80	9	17)	
Ethanol– <i>n</i> –Heptane	760	71.0 – 98.4	34	35	33	2.0	2.1	1.8	18	14)	
<i>n</i> –Propanol– <i>n</i> –Hexane	760	65.7 – 97.2	42.4	42.5	44.0	1.5	1.5	1.6	12	23)	
<i>n</i> –Propanol– <i>n</i> –Heptane	760	84.6 – 98.4	17	17	18	0.9	0.9	0.9	9	10)	
<i>n</i> –Butanol– <i>n</i> –Octane	760	108.5 –125.7	26	27	33	0.8	0.9	1.5	10	15)	
<i>n</i> –Butanol– <i>n</i> –Nonane	760	115.9 –150.8	7	8	13	0.4	0.5	1.2	9	15)	
Ethanol–Benzene	760	67.9 – 80.1	31	31	36	2.5	2.5	2.8	10	21)	
<i>n</i> –Propanol–Benzene	760	76.0 – 97.2	54	53	56	1.7	1.7	1.9	12	23)	
<i>n</i> –Butanol– <i>n</i> –Heptane	1,445	114.8 –137.0	25	26	33	1.1	1.2	2.2	10	30)	
Methanol–Water	3,800	112.2 –152.3	9.9	10.0	13.0	1.3	1.3	1.7	22	12)	5 atm
Methanol–Water	6,080	129.1 –169.5	11.5	11.7	14.6	1.2	1.1	1.7	22	12)	8 atm
Methanol–Water	8,512	142.0 –185.4	14.0	14.5	16.5	1.1	1.0	1.8	22	12)	11.2atm
Ethanol–Water	2,586	112.6 –134.6	9	10	8	0.3	0.3	0.9	18	22)	50 psia
Ethanol–Water	5,172	136.7 –164.2	19	21	10	1.2	1.3	0.4	18	22)	100 psia
Ethanol–Water	10,344	164.2 –194.1	30	32	17	2.2	2.5	0.7	18	22)	200 psia
Ethanol–Water	15,512	182.6 –213.8	41	45	23	3.2	3.5	1.0	17	22)	300 psia

*T. K = by Tochigi and Kojima's parameters *D. D = by Derr and Deal's parameters *N = No. of data points

Fig. 2 Temperature-Composition Diagram for *i*-Propanol (1)-*n*-Propanol (2) System at 760 mmHg

Fig. 3 Temperature-Composition Diagram for *n*-Butanol (1)-*n*-Nonane (2) System at 760 mmHg

group.

Figs. 1 to 4 show the predicted vapor-liquid equilibria with the experimental temperature vs. liquid composition data for ethanol-water, *i*-pro-

Fig. 4 Temperature-Composition Diagram for Methanol (1)-Water (2) System at 11.2 atm

panol-*n*-propanol, *n*-butanol-*n*-nonane, and methanol-water systems, respectively.

The predicted results in **Table 3** and **Figs. 1 to 4** show good agreement with those of the experiments.

5 Prediction of Solid-Liquid Equilibria

Solid-liquid equilibria considered in this paper are those for 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. Thus, the liquid phase activity coefficients for the solute component *i* of solid-liquid equilibria were calculated using the simple Van't Hoff isochore equation which is given by Eq. (16).

$$\ln \gamma_i x_i = \frac{\Delta H_i}{RT} - \frac{(T - T_i^M)}{T_i^M} \quad (16)$$

where ΔH_i is the heat of fusion of the solute component *i*, *R* is the gas constant and T_i^M is the temperature of melting point of the solute component *i*. Eq. (16) can be written for liquid composition of the solute component *i*, as follows:

$$x_i = \exp \left(\frac{\Delta H_i}{RT} - \frac{(T - T_i^M)}{T_i^M} - \ln \gamma_i \right) \quad (17)$$

The activity coefficients in Eq. (17) are predicted by using Eqs. (1) to (6).

The predicted results for solid-liquid equilibria of naphthalene-alcohol systems are listed in **Table 4** with the absolute arithmetic mean deviations

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.
Naphthalene-Ethanol	55.3	20.0-80.0	11	2)
Naphthalene- <i>n</i> -Propanol	38.4	20.0-80.0	11	2)
Naphthalene- <i>i</i> -Propanol	45.3	20.0-80.0	11	2)
Naphthalene- <i>n</i> -Butanol	31.8	25.0-80.0	10	2)
Naphthalene- <i>i</i> -Butanol	30.1	20.0-80.0	11	2)

* $\Delta x_1 = [|(x_{1,exp} - x_{1,cal})| / N] \times 1,000$

*N=No. of data points

Fig. 5 Solubility Diagram of Solid Naphthalene in Liquid Phase for Naphthalene (1)-*n*-Butanol (2) System

between observed and predicted liquid compositions obtained by means of our parameters. **Fig. 5** shows the predicted solid-liquid equilibria with the experimental temperature vs. liquid composition data for the naphthalene-*n*-butanol system. Assuming the systems ideal, i.e. γ_i in Eqs. (16) and (17) are taken to be 1.0, the calculated values are also plotted in Fig. (5).

The predicted solid-liquid equilibrium data shown in **Table 4** and **Fig. 5** indicated good agreement with the experimental data.

In this study, 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.

6 Conclusions

The group Wilson parameters to predict liquid phase activity coefficients by the ASOG model for the systems consisting of CH_2 and OH groups were determined using the isothermal vapor-liquid equilibrium data of the alcohol-water and alcohol-paraffin systems at temperatures 30, 50, 60 and 90°C. The isobaric vapor-liquid equilibria of the binary systems involving alcohols, water, paraffins

and benzene were successfully predicted even within the temperature range from 90°C to 215°C and the pressures up to 20 atm. Also, the prediction of binary solid-liquid equilibria of the naphthalene-alcohol systems showed good agreement with those of the experimental data.

Acknowledgment

The authors express their thanks to Mr. Masaru Toyohara for his assistance in the computational work.

Nomenclature

a	=group Wilson parameter	[—]
ΔH	=heat of fusion	[cal/g-mol]
P	=vapor pressure	[mmHg]
R	=gas constant	[cal/g-mol·k]
T	=absolute temperature	[K]
U	=solute group ratio	[—]
X	=group fraction	[—]
x	=mole fraction in liquid phase	[—]
y	=mole fraction in vapor phase	[—]
Γ	=group activity coefficient	[—]
γ	=activity coefficient	[—]
π	=total pressure	[mmHg]
ν	=number of groups	[—]

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

Superscripts

- FH=size contribution
G=group contribution
M=melting point

Literature Cited

- 1) Amer, H. H., Paxton, R. R., van Winkle, M., *Ind. Eng. Chem.*, **48**, 142 (1956).
- 2) Arthur, A. S., *J. Phys. Chem.*, **34**, 2582 (1930).
- 3) Ballard, L. H., van Winkle, M., *Ind. Eng. Chem.*, **44**, 2450 (1952).
- 4) Benedict, M., Johnson, A., Solomon, E., Rubin, L. C., *Trans. Am. Inst. Chem. Eng.*, **41**, 371 (1945).
- 5) Broul, M., Hlavaty, K., Linek, J., *Collection Czech. Chem. Commun.*, **34**, 3428 (1969).
- 6) Carey, J. S., Lewis, W. K., *Ind. Eng. Chem.*, **24**, 882 (1932).
- 7) Chu, Ju Chin, Getty, R. J., Brennecke, L. F., Paul, R., *Distillation Equilibrium Data*, Reinhold, (1950).
- 8) Derr, E. L., Deal, C. H., *I. Chem. E. Symposium Series*, **32**, P. 3: 40 (1969).
- 9) Dulitskaya K. A., *Zh. Obshch. Khim.*, **15**, 9 (1945).
- 10) Gurukul, S. M. K. A., Raju, B. N., *J. Chem. Eng.*

- Data*, **11**, 501 (1966).
- 11) Hellwig, L. R., van Winkle, M., *Ind. Eng. Chem.*, **45**, 624 (1953).
 - 12) Hirata M., Suda, S., *Kagaku Kogaku*, **31**, 759 (1967).
 - 13) Ishii, N., *Kogyo Kagaku Zasshi*, **38**, 659 (1935).
 - 14) Katz, K., Newman, M., *Ind. Eng. Chem.*, **48**, 137 (1956).
 - 15) Kogan, V. B., Fridman, V. M., Romanovai, T. G., *Zh. Fiz. Khim.*, **29**, 685 (1955).
 - 16) Kojima, K., Kato, M., Sunaga, H., Hashimoto, S., *Kagaku Kogaku*, **32**, 337 (1968).
 - 17) Kudryavtseva, L. S., Susarev, M. P., *Zh. Prikl. Khim.*, **36**, 1231 (1963).
 - 18) Maripuri, V. C., Ratcliff, G. A., *Canadian J. Chem. Eng.*, **49**, 506 (1971).
 - 19) Mcglashan, M. L., Williamson, A. G., *J. Chem. Eng. Data*, **21**, 196 (1976).
 - 20) Murti, P. S., van Winkle, M., *Chem. Eng. Data Series*, **3**, 72 (1958).
 - 21) Niini, A., *Ann. Acad. Sci. Fenn.*, **A 55**, No. 8 (1940).
 - 22) Otsuki, H., Williams, F. C., *Chem. Eng. Prog. Symp. Series*, **49**, (6), 55 (1953).
 - 23) Parabhu, P. S., van Winkle, M., *J. Chem. Eng. Data*, **8**, 210 (1963).
 - 24) Ratcliff, G. A., Chao, K. C., *Canadian J. Chem. Eng.*, **47**, 148 (1969).
 - 25) Ronc, M., Ratcliff, G. A., *ibid.*, **49**, 825 (1971).
 - 26) Smith, C. P., Engel, E. W., *J. Am. Chem. Soc.*, **51**, 2660 (1929).
 - 27) Tochigi, K., Kojima, K., *J. Chem. Eng. Japan*, **9**, (4), 267 (1976).
 - 28) Udovenko, V. V., Fatkulina, L. G., *Zh. Fiz. Khim.*, **26**, 1438 (1952).
 - 29) van Ness, H. C., Soczek, C. A., Peloquin, G. L., Machado, R. L., *J. Chem. Eng. Data*, **12**, 217 (1967).
 - 30) Vijayaraghavan, S. V., Deshpande, P. K., Kuloor, N. R., *ibid.*, **12**, 15 (1967).
 - 31) Wilson, G. M., Deal, C. H., *Ind. Eng. Chem. Fundamentals*, **1**, 20 (1962).
 - 32) Wreowsky, M. S., *Z. Phys. Chem.*, **81**, 1 (1912).
-