PREDICTION OF VAPOR-LIQUID EQUILIBRIA WITH CHEMICAL REACTION BY ANALYTICAL SOLUTIONS OF GROUPS

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To discuss prediction of vapor-liquid equilibria with esterification on the basis of the ASOG model, infinite-dilution binary activity coefficients were measured for five systems in the 40°–100°C range by an ebulliometric method. The systems measured are methyl acetate–*n*-heptane, ethyl acetate–ethanol, ethyl acetate–water, acetic acid–*n*-heptane, and acetic acid–ethyl acetate. The group Wilson parameters for any system made up of CH₃, OH, COO, COOH groups were determined in the 40°–100°C range by infinite-dilution activity coefficients. Vapor-liquid equilibria predicted for three quaternary esterification systems and for 26 binary and ternary systems involving alcohols, water, paraffins, esters, and carboxylic acids agreed fairly well with observed values.

Introduction

Extensive studies of experimental and theoretical aspects of vapor-liquid equilibria have been undertaken in the past, though mostly on systems in which no chemical reaction occurs. Apparently, few studies of vapor-liquid equilibria of systems in which chemical reaction occurs in liquid phase, such as esterification, have been made. Komatsu, Hirata *et al.*^{11–13)} observed vapor-liquid equilibria of quaternary systems, like acetic acid–alcohols–water–esters, with esterification and proposed an empirical method for correlating vapor-liquid equilibria with esterification by using vapor-liquid equilibrium ratio. Nishi²¹⁾ observed vapor-liquid equilibria for the acetic acid–*i*-propanol–water–*i*-propyl acetate system and showed that the data could be correlated satisfactorily by the method of Komatsu, Hirata *et al.*, Suzuki, Komatsu and Hirata³⁵⁾ tried to correlate vapor-liquid equilibria with esterification on the basis of activity coefficient equations for the purpose of developing an empirical method.

An ASOG (Analytical Solutions of Groups) model constitutes a predictive method^{5,8,36)} for obtaining activity coefficients. It is a widely applicable method requiring minimum experimental data and is of practical use in predicting vapor-liquid and liquid-liquid equilibria. Derr and Deal⁵⁾ suggested application of ASOG to reaction systems. Hardly any studies seems to have been reported, however, for concrete application of ASOG to reaction systems.

The present paper deals with prediction of vapor-

liquid equilibria with esterification by ASOG model. Here, the group Wilson parameters for any system made up of CH₃, OH, COO, COOH groups were determined first in the 40°–100°C range by the ebulliometric method. Next, by applying the group Wilson parameters, prediction of vapor-liquid and vapor-liquid-liquid equilibria was made for 22 binary systems constituted by CH₃–COO, CH₃–OH–COO, CH₃–OH–COOH, CH₃–COO–COOH groups and four ternary systems constituted by CH₃–OH–COO groups. Further prediction of vapor-liquid equilibria with esterification has been made for the acetic acid–ethanol–water–ethyl acetate, acetic acid–*i*-propanol–water–*i*-propyl acetate and acetic acid–*n*-butanol–water–butyl acetate systems.

1. Measurement of Infinite Dilution Activity Coefficients

Group Wilson parameters necessary for predicting vapor-liquid equilibria with esterification by using ASOG are those relating to the six group pairs (made up of CH₃, OH, COO and COOH groups) CH₃–COO, OH–COO, CH₃–COOH, OH–COOH, COO–COOH, CH₃–OH. For the sake of simplicity, no distinction is made between CH₃ and CH₂ groups^{27,31)}.

Several attempts^{30,34,36)} have been made for experimentally determining group Wilson parameters. In the previous study³⁶⁾, the authors discussed the method for determining the parameters by infinite dilution activity coefficients measured by using ebulliometer and determined group Wilson parameters for any system made up of CH₃, OH, CO groups in the 40°–100°C range. The infinite dilution activity co-

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Table 1 Observed binary activity coefficients at infinite dilution

System	γ_1^∞	40	60	80	100
Methyl acetate (1)	γ_1^∞	3.63	3.80	3.99	4.19
<i>n</i> -Heptane (2)	γ_2^∞	4.82	5.12	5.37	5.58
Ethyl acetate (1)	γ_1^∞	2.77	2.53	2.25	1.94
Ethanol (2)	γ_2^∞	3.29	2.82	2.44	2.14
Ethyl acetate (1)	γ_1^∞	—	—	—	—
Water (2)	γ_2^∞	11.88	10.40	9.23	8.32
Acetic acid (1)	γ_1^∞	24.66	18.86	18.11	17.50
<i>n</i> -Heptane (2)	γ_2^∞	10.57	11.30	12.74	15.14
Acetic acid (1)	γ_1^∞	1.22	1.40	1.57	1.75
Ethyl acetate (2)	γ_2^∞	1.17	1.21	1.25	1.29

efficients for a binary system consisting of acetic acid, a self-associating component, and water were measured³⁸⁾ in the 60°C–110°C range.

In the present study, infinite dilution activity coefficients have been measured for five binary systems made up of CH₂, OH, COO, COOH groups by the ebulliometric method. The experimental apparatus used is the same as that in the previous paper³⁸⁾. The systems measured are methyl acetate–*n*-heptane (CH₂–COO system), ethyl acetate–ethanol, ethyl acetate–water (CH₂–OH–COO systems), acetic acid–*n*-heptane (CH₂–COOH system), acetic acid–ethyl acetate (CH₂–COO–COOH system). Bubble points were measured for about 15 compositions at 760, 600, 400, 200, 150 mm of Hg and at intervals of about 2 mol% in the dilute regions (less than 10 mol%, greater than 90 mol%). For a heterogeneous liquid system of ethyl acetate–water, the bubble points were measured in a region in which concentration of ethyl acetate is rich. The bubble points were not measured in the ethyl acetate–dilute region, because a two-liquid phase was formed in the region of less than about 3 mole% ethyl acetate. Infinite dilution activity coefficients were obtained for water in ethyl acetate alone.

Reagents other than water used in the experiments were of special grade (Wako Pure Chem. Ind. Ltd.). Distilled water was used after ion exchange.

Measurement of infinite dilution binary activity coefficients from *T*-*x* data for the three binary systems constituted by ethyl acetate (1)–*n*-heptane (2), ethyl acetate (1)–ethanol (2), ethyl acetate (1)–water (2) is based on calculations using Eqs. (1) and (2)^{10,16)}.

$$\gamma_1^\infty = (P/P_1^0)\{1 - (\partial T/\partial x_1)(d \ln P_2^0/dT)\}_{x_1=0} \quad (1)$$

$$\gamma_2^\infty = (P/P_2^0)\{1 - (\partial T/\partial x_2)(d \ln P_1^0/dT)\}_{x_2=0} \quad (2)$$

Assuming that the formation of higher aggregates than dimer for acetic acid is negligible in the vapor phase, Eqs. (3) and (4) below, derived earlier³⁸⁾, were applied for computing the infinite dilution activity coefficients for two binary systems containing acetic acid (which is a self-associating component): acetic

acid (1)–*n*-heptane (2) and acetic acid (1)–ethyl acetate (2). Thus

$$\gamma_1^\infty = (P/P_1^0)\{1 - (\partial T/\partial x_1)(d \ln P_2^0/dT)\}_{x_1=0} \quad (3)$$

$$\gamma_2^\infty = (P/P_2^0)\{[1 - (\partial T/\partial x_2)(d \ln P_1^0/dT)](2 - \eta_1) - (\partial T/\partial x_2)(d \ln K_2/dT)(1 - \eta_1)\}_{x_2=0} \quad (4)$$

where P_1^0 and P_2^0 denote, respectively, the vapor pressures of acetic acid monomer³⁸⁾ and component 2, and K_2 represents the vapor-phase association constant of dimerization for acetic acid, calculated on the basis of the data²⁸⁾ obtained from Ritter *et al.* As for η_1 , it is the true mole fraction of acetic acid monomer in vapor phase and is calculated^{17,38)} by applying Eq. (5).

$$\eta_1 = (-1 + \sqrt{1 + 4K_2P})/2K_2P \quad (5)$$

Terminal slopes for the *T*-*x* curve, $(\partial T/\partial x_1)_{x_1=0}$, $(\partial T/\partial x_2)_{x_2=0}$ were evaluated by the Ellis and Jonah method⁷⁾. Vapor pressures for pure materials are calculated by applying the Antoine equation. Thus

$$d \ln P_i^0/dT = 2.303B_i/(t^\circ\text{C} + C_i)^2 \quad (6)$$

Table 1 shows the infinite dilution binary activity coefficients for components 1 and 2 in the 40°–100°C range by applying Eqs. (1) and (2) for the methyl acetate–*n*-heptane, ethyl acetate–ethanol, ethyl acetate–water systems and by applying Eqs. (3) and (4) for the acetic acid–*n*-heptane, acetic acid–ethyl acetate systems.

2. Determination of Group Wilson Parameters

On the basis of the ASOG (Analytical Solutions of Groups) model^{15,30,36)}, the activity coefficients are calculated with the help of Eqs. (7) to (9).

$$\log \gamma_i = \log \gamma_i^{\text{FH}} + \log \gamma_i^{\text{G}} \quad (7)$$

$$\log \gamma_i^{\text{FH}} = \log \{ \nu_i^{\text{FH}} / (\sum_{j=1}^n x_j \nu_j^{\text{FH}}) \} + 0.434 \{ 1 - \nu_i^{\text{FH}} / (\sum_{j=1}^n x_j \nu_j^{\text{FH}}) \} \quad (7a)$$

$$\log \gamma_i^{\text{G}} = \sum_k \nu_{ki} (\log \Gamma_k - \log \Gamma_k^{(i)}) \quad (7b)$$

$$\log \Gamma_k = -\log \sum_l X_l a_{k/l} + 0.434 [1 - \sum_l \{ X_l a_{l/k} / (\sum_m X_m a_{l/m}) \}] \quad (8)$$

$$X_k = \sum_{i=1}^n x_i \nu_{ki} / \sum_{i=1}^n x_i \sum_k \nu_{ki} \quad (9)$$

where ν_i^{FH} represents the number of atoms (other than the hydrogen atoms) in the molecular species *i*, and ν_{ki} is the number of interaction groups of kind *k* in molecule *i*. The entities Γ_k and X_k represent, respectively, the group activity coefficient and the group fraction of group *k*. As for $a_{k/l}$, $a_{l/k}$, these are group Wilson parameters. Activity coefficients are calculated by substituting known values of $a_{k/l}$, $a_{l/k}$ in Eqs. (7) to (9).

As for the method of determining the group Wilson

Table 2 Constants $m_{k/l}$ and $n_{k/l}$ in Eq. (10) (40°–100°C)

k	l	CH ₂		OH		COO		COOH	
		$m_{k/l}$	$n_{k/l}$	$m_{k/l}$	$n_{k/l}$	$m_{k/l}$	$n_{k/l}$	$m_{k/l}$	$n_{k/l}$
CH ₂		0	0	−0.4962	−11.2	−0.1209	18.1	−0.3307	150.6
OH		0.6007	−767.1	0	0	0.1616	−286.1	0.7907	−418.6
COO		−0.3730	41.5	−0.0615	52.5	0	0	1.2470	−363.1
COOH		0.1364	−265.6	−0.5256	223.3	−2.2885	690.0	0	0

parameters on the basis of infinite dilution activity coefficients, this consists of calculation of twelve group Wilson parameters made up of the six group pairs CH₂–COO, OH–COO, CH₂–COOH, OH–COOH, COO–COOH, CH₂–OH under the condition of constant temperature as follows: First the group Wilson parameters for CH₂–COO system are determined on the basis of the infinite dilution activity coefficients of methyl acetate–*n*-heptane. The number ν_{COO} of COO groups in methyl acetate used in the calculation is 3, i.e. $\nu_{\text{COO}}=3$. This value is the same as that used by Derr and Deal⁵⁾. The group Wilson parameters for OH–COO system are calculated on the basis of the infinite dilution activity coefficients of ethyl acetate–ethanol and ethyl acetate–water by using known values of $a_{\text{CH}_2/\text{OH}}$, $a_{\text{OH}/\text{CH}_2}$ obtained in the previous paper³⁶⁾. The water molecule is treated³⁶⁾ as 1.6 interaction hydroxyl groups. The group Wilson parameters for CH₂–COOH system are calculated on the basis of the infinite dilution activity coefficients of acetic acid–*n*-heptane. The number ν_{COOH} of COOH groups in acetic acid used in the calculation is 3, i.e. $\nu_{\text{COOH}}=3$. The group Wilson parameters for COO–COOH system are calculated on the basis of the infinite dilution activity coefficients of acetic acid–ethyl acetate by using known values of $a_{\text{CH}_2/\text{COOH}}$, $a_{\text{COOH}/\text{CH}_2}$. The group Wilson parameters for OH–COOH system are calculated by using known values of $a_{\text{CH}_2/\text{OH}}$, $a_{\text{OH}/\text{CH}_2}$, $a_{\text{CH}_2/\text{COOH}}$, $a_{\text{COOH}/\text{CH}_2}$ on the basis of the infinite dilution activity coefficients of acetic acid–water given in the previous paper³⁸⁾.

Figure 1 shows group Wilson parameters (determined at 40°, 60°, 80° and 100°C) plotted against the temperature. As is evident from the figure, the logarithms of group Wilson parameters are inversely proportional to the absolute temperature in the temperature range in this work. Therefore

$$\log a_{k/l} = m_{k/l} + n_{k/l}/T \quad (10)$$

where $m_{k/l}$ and $n_{k/l}$ are constants with respect to group pairs. Table 2 shows the constants $m_{k/l}$ and $n_{k/l}$ for any system made up of CH₂, OH, COO, COOH groups. In Table 2, the constants for the CH₂–OH system obtained in the previous paper³⁶⁾ are also shown.

3. Prediction of Vapor-Liquid Equilibria for Binary and Ternary Systems

Fig. 1 Variation of group Wilson parameters with temperature

Prediction on vapor-liquid equilibria with esterification has been preceded by that on vapor-liquid equilibria using the group Wilson parameters for 22 isobaric binary systems (Table 3) constituted by CH₂–COO, CH₂–OH–COO, CH₂–OH–COOH, CH₂–COO–COOH groups and four isobaric ternary systems (Table 4) constituted by CH₂–OH–COO groups. The systems discussed include those with two liquid phases, namely ethyl acetate–water, water–propyl acetate (Nos. 12, 13 in Table 3), *n*-propanol–propyl propionate–water, methyl acetate–methanol–water (Nos. 3, 4 in Table 4), and nine binary systems (Nos. 14–22 in Table 3) containing acetic and propionic acids, both of which are self-associating components in vapor phase. Thus, calculation for the vapor-liquid equilibria is carried out on the basis of Eqs. (11) to (13), derived with a view to applying them to ordinary and heterogeneous liquid systems²⁶⁾, as well as to systems with a self-associating component in vapor phase.

$$\eta_i = \gamma_i^I P_i^0 x_i^I / P = \gamma_i^{II} P_i^0 x_i^{II} / P \quad (11)$$

$$\eta_1 + \eta_{12} + \sum_{i=2}^n \eta_i = 1, \quad \eta_{12} = K_2 P \eta_1^2 \quad (12)$$

Table 3 Deviations of predicted values from observed vapor-liquid equilibria for binary systems

No.	System		Press. [mmHg]	No. of data points	Absolute arithmetic deviations in $y_1 \times 1000$ t [°C]		Ref.
	Component (1)	Component (2)					
Group $\text{CH}_2 + \text{COO}$							
1	Methyl formate	<i>n</i> -Hexane	760	14	10	1.57	23
2	Ethyl acetate	Butyl acetate	"	13	8	0.49	32
Group $\text{CH}_2 + \text{OH} + \text{COO}$							
3	Methanol	Methyl acetate	760	7	14	1.31	6
4	Methanol	Ethyl acetate	"	19	11	0.99	1
5	Ethyl acetate	Ethanol	"	12	6	0.47	15
6	Ethyl acetate	<i>n</i> -Propanol	"	14	18	1.00	20
7	Ethyl acetate	<i>n</i> -Butanol	"	16	16	1.47	32
8	Propyl acetate	<i>n</i> -Propanol	"	11	7	0.45	26
9	<i>n</i> -Butanol	Butyl acetate	"	24	8	0.52	3
10	Propyl formate	<i>n</i> -Propanol	"	6	36	—	18
11	<i>n</i> -Propanol	Propyl propionate	"	7	26	1.79	"
12*	Ethyl acetate	Water	"	22	49	1.80	15
13*	Water	Propyl acetate	"	7	49	2.37	33
Group $\text{CH}_2 + \text{OH} + \text{COOH}$							
14	Acetic acid	Water	760	16	10	1.18	14
15	Propionic acid	Water	"	9	21	0.96	2
16	Acetic acid	Methanol	706	20	21	1.23	29
17	Acetic acid	Ethanol	"	16	27	1.91	"
18	Acetic acid	<i>n</i> -Propanol	"	14	27	2.60	"
19	Acetic acid	<i>n</i> -Butanol	"	18	30	2.28	"
Group $\text{CH}_2 + \text{COO} + \text{COOH}$							
20	Acetic acid	Ethyl acetate	760	6	9	0.69	9
21	Acetic acid	Propyl acetate	"	10	23	—	24
22	Acetic acid	Butyl acetate	"	10	15	—	"

* heterogeneous liquid system

Table 4 Deviations of predicted values from observed vapor-liquid equilibria for ternary systems (760 mm of Hg)

No.	System			No. of data points	Absolute arithmetic deviations in $y_1 \times 1000$ $y_2 \times 1000$ t [°C]			Ref.
	Component (1)	Component (2)	Component (3)					
Group $\text{CH}_2 + \text{OH} + \text{COO}$								
1	Ethyl acetate	Ethanol	Butyl acetate	77	23	12	0.38	32
2	Ethyl acetate	Ethanol	<i>n</i> -Butanol	88	34	11	1.05	"
3*	<i>n</i> -Propanol	Propyl propionate	Water	19	65	30	1.02	19
4*	Methyl acetate	Methanol	Water	32	43	23	2.27	4

* heterogeneous liquid system

$$\left. \begin{aligned} y_1 &= (\eta_1 + 2\eta_{12}) / (\eta_1 + 2\eta_{12} + \sum_{i=2}^n \eta_i) \\ y_j &= \eta_j / (\eta_1 + 2\eta_{12} + \sum_{i=2}^n \eta_i) \end{aligned} \right\} \quad (13)$$

In the above equations it has been assumed that the formation of higher aggregates than dimer for an associating component is negligible in vapor phase. Also, x_i^I and x_i^{II} are, respectively, the mole fraction of component i in the two liquid phases I and II in equilibrium and are evaluated^{22,37)} from the conditions of liquid-liquid equilibria by a modified Newton-Raphson method. It naturally follows that in the region where a system becomes one constituted by a single liquid phase $x_i^I = x_i^{II} = x_i$, $\gamma_i^I = \gamma_i^{II} = \gamma_i$. In the equations η_i represents true mole fraction in the vapor phase and subscripts 1 and 12 denote, respectively, an associating component monomer and a dimer. When applied to a system not containing associating components like acetic acid or propionic

acid, $\eta_{12} = 0$, $\eta_1 = y_1$ and $\eta_j = y_j$. Activity coefficients are predicted by applying Eqs. (7) to (10) on the basis of the ASOG model.

Prediction of vapor-liquid equilibria has been made on the basis of an ASOG model for 22 isobaric binary systems. Table 3 shows the deviations between predicted and observed vapor compositions and bubble points. As indicated in Table 3, the results agree fairly well with observed values. **Figures 2 to 5** compare predicted and observed vapor compositions for the ethyl acetate-ethanol, acetic acid-water, acetic acid-methanol and ethyl acetate-water systems.

Prediction of vapor-liquid equilibria was made for four isobaric ternary systems. A comparison of predicted and observed vapor compositions and bubble points appears in Table 4.

4. Prediction of Quaternary Vapor-Liquid Equilibria with Esterification

Fig. 2 Vapor-liquid equilibria for ethyl acetate (1)-ethanol (2) system at 760 mm of Hg

Fig. 4 Vapor-liquid equilibria for acetic acid (1)-methanol (2) system at 706 mm of Hg

Fig. 3 Vapor-liquid equilibria for acetic acid (1)-water (2) system at 760 mm of Hg

Fig. 5 Vapor-liquid equilibria for ethyl acetate (1)-water (2) system at 760 mm of Hg

Table 5 Deviations of predicted values from observed vapor-liquid equilibria for quaternary systems with esterification (760 mm of Hg)

No.	Component (1)	Component (2)	System Component (3)	Component (4)	No. of data points	Absolute arithmetic deviations in $y_i \times 1000$				t [°C]	Ref.
						y_1	y_2	y_3	y_4		
1	Acetic acid	Ethanol	Water	Ethyl acetate	270	12	11	21	21	1.47	12
2	Acetic acid	<i>i</i> -Propanol	Water	<i>i</i> -Propyl acetate	243	12	26	28	33	1.52	21
3	Acetic acid	<i>n</i> -Butanol	Water	Butyl acetate	143	22	14	34	19	2.16	11

Prediction of vapor-liquid equilibria with esterification was made on the basis of an ASOG model for three isobaric quaternary systems, acetic acid-ethanol-water-ethyl acetate, acetic acid-*i*-propanol-water-*i*-propyl acetate, and acetic acid-*n*-butanol-water-butyl acetate. It has been pointed out^{11,12,21)} that these esterification systems have two liquid phase regions within a range of approximately 70°–100°C. Further, they contain acetic acid, an associating component in vapor phase. Therefore, calculation for vapor-liquid equilibria is carried out on the basis of Eqs. (11) to (13), which appeared earlier and which are applicable to systems having two liquid phases and a vapor associating component. Activity coefficients are calculated on the basis of ASOG from Eqs. (7) to (10) using the constants shown in Table 2.

Table 5 shows the deviations between predicted and observed vapor compositions and bubble points for

three esterification systems. The observed values employed for comparison with the predicted ones are those obtained by Komatsu, Hirata *et al.*^{11,12)} for the acetic acid-ethanol-water-ethyl acetate and acetic acid-*n*-butanol-water-butyl acetate systems and by Nishi²¹⁾ (values evaluated by correlation¹²⁾) for the acetic acid-*i*-propanol-water-*i*-propyl acetate system.

Conclusion

To discuss prediction of vapor-liquid equilibria with esterification on the basis of the ASOG model, the group Wilson parameters for any system made up of CH₃, OH, COO, COOH groups were determined in the 40°–100°C range by an ebulliometric method. By using the parameters so determined, vapor-liquid equilibria predicted for three quaternary esterification systems and 26 binary and ternary systems involving alcohols, water, paraffins, esters and carboxylic acids

agreed well with observed values.

Nomenclature

a	= group Wilson parameter	[—]
B, C	= constants of Antoine equation	[—]
K_2	= vapor-phase association constant of dimer	[mmHg ⁻¹]
m, n	= constants in Eq. (10)	[—]
P^0	= vapor pressure	[mmHg]
P	= total pressure	[mmHg]
T	= absolute temperature	[°K]
t	= temperature	[°C]
X	= group fraction	[—]
x	= mole fraction in liquid phase	[—]
y	= stoichiometric mole fraction in vapor phase	[—]
Γ	= group activity coefficient	[—]
γ	= activity coefficient	[—]
η	= true mole fraction in vapor phase	[—]
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>

I, II	= liquid phase I and II
i	= standard state
FH	= size contribution
G	= group contribution
∞	= infinite dilution

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