Measurement of Isothermal Vapor−Liquid Equilibria for Monocarboxylic Acid + Monocarboxylic Acid Binary Systems with a Flow-Type Apparatus

Shinji Miyamoto and Shinichi Nakamura

Idemitsu Petrochemical Company, Ltd., 1-1 Shingu-cho, Tokuyama, Yamaguchi 745-0843, Japan

Yoshio Iwai* and Yasuhiko Arai

Department of Chemical Systems and Engineering, Graduate School of Engineering, Kyushu University,
6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

A flow-type apparatus was constructed to measure isothermal vapor−liquid equilibria. The reliability of this experimental method was confirmed by comparing the data obtained with literature values. Isothermal vapor−liquid equilibria for the five monocarboxylic acid + monocarboxylic acid binary systems (formic acid + acetic acid, formic acid + propionic acid, acetic acid + propionic acid, acetic acid + butyric acid, and propionic acid + butyric acid) were measured. The experimental data obtained in this work were correlated by applying the NRTL model to liquid-phase activity coefficients and by assuming vapor-phase association between monocarboxylic acids.

Introduction

Vapor-phase association affects physical properties of mixtures containing carboxylic acids. For example, vapor−liquid equilibria are significantly affected. In the compilation of Gmehling and Onken,[1] only two sets of vapor−liquid equilibria data for monocarboxylic acid + monocarboxylic acid binary systems are thermodynamically consistent. Further, it is shown that there are few data sets for isothermal vapor−liquid equilibria of systems containing a monocarboxylic acid which are useful for a consideration of the association effect. Therefore, we have investigated the effect of association on isothermal vapor−liquid equilibria. In a previous work,[2] vapor−liquid equilibrium data for hydrocarbon + monocarboxylic acid binary systems were measured with a flow apparatus. In this work, the vapor−liquid equilibrium data for monocarboxylic acid + monocarboxylic acid binary systems were measured. The previous apparatus was improved by changing the method for sampling the vapor phase to determine the vapor-phase composition more precisely. The new apparatus was tested with measurement of vapor−liquid equilibria for the ethanol + toluene binary system at 323.2 K. Then, isothermal vapor−liquid equilibria for five monocarboxylic acid + monocarboxylic acid binary systems were measured. Mixtures of formic acid + acetic acid, formic acid + propionic acid, and acetic acid + propionic acid were measured at 343.2 K and mixtures of acetic acid + butyric acid and propionic acid + butyric acid binary systems at 358.2 K. Further, they were correlated by applying the NRTL model to liquid-phase activity coefficients and by assuming vapor-phase association between monocarboxylic acids.

Experimental Section

Materials. All chemicals used in this study were guaranteed reagent grade. The purities of chemicals were reported by the supplier, Kishida Chemical Co., as follows: higher than 98.0% for formic acid; 99.7% for acetic acid; 99.5% for propionic acid, ethanol, and toluene; and, 99.0% for butyric acid. Formic acid was purified by fractional freezing; its final purity was more than 99.7% as determined by gas chromatography with a thermal conductivity detector. Other chemicals were used without further purification. The parameters of the Antoine equation[3,4] for the chemicals used are presented in Table 1. The purity of helium used as a carrier gas was reported by the supplier, Nippon Sanso Co., to be higher than 99.995%.

Apparatus. A flow-type apparatus was previously constructed[2] to measure the isothermal vapor−liquid equilibria. The apparatus was improved in this work by changing the sampling method to determine vapor-phase compositions more precisely. The schematic diagram of the apparatus is shown in Figure 1. The apparatus consisted of a carrier gas cylinder, a mass flow controller, an equilibrium glass cell (about 30 mL), a water bath (controlled within ±0.05 K), a thermometer (with an uncertainty of ±0.05 K), a condensation glass cell, and a dry ice−2-propanol bath. Helium gas was used as a carrier gas because it is inert and has a high thermal conductivity. A connecting line from the equilibrium cell to the condensation cell was heated and maintained at 50 K higher than the temperature of the water bath (323.2, 343.2, and 358.2 K) to avoid any condensation. The temperature of the condensation cell was maintained between 200 and 230 K.

Procedures. A binary liquid mixture (about 20 g) of known composition was charged into the equilibrium cell. The cell was weighed by an electronic balance (uncertainty ±0.0002 g). The equilibrium cell and the preheating line were immersed in the water bath, and the condensation cell was placed in the dry ice−2-propanol bath. After the temperature of the sample reached that of the water bath,

---

* To whom correspondence should be addressed. E-mail: iwai@chem-eng.kyushu-u.ac.jp. Fax: +81 92 642 3496.

10.1021/je000205n CCC: $20.00

Table 1. Antoine Constants[a] for Saturated Vapor Pressures

	A	B	C
ethanol[b]	16.896 59	3803.986	41.670
toluene[b]	13.998 42	3096.516	53.668
formic acid[c]	15.405 60	3894.764	13.000
acetic acid[c]	15.192 34	3654.622	45.392
propionic acid[c]	15.296 86	3670.949	70.545
butyric acid[c]	15.096 74	3599.963	93.307

[a] $\ln(p^{\mathrm{sat}}/\mathrm{kPa}) = A - B/[(T/\mathrm{K}) - C]$. [b] Yaws.[3] [c] Ambrose and Ghiassee.[4]

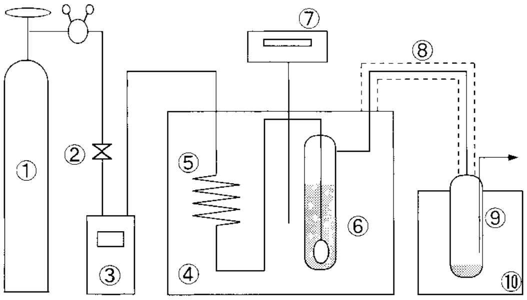

Figure 1. Schematic diagram of flow-type apparatus: (1) carrier gas cylinder; (2) mass flow controller; (3) flowmeter; (4) water bath; (5) heat exchanger; (6) equilibrium cell; (7) thermometer; (8) ribbon heater; (9) condensation cell; (10) dry ice−2-propanol bath.

helium gas was flowed into the cell. Helium gas was slowly passed (about 30 mL·min^{-1}) through the liquid mixture to establish equilibrium. Helium gas containing the vapor-phase components passed through the condensation cell and discharged into the atmosphere. When the vapor phase in the equilibrium cell was carried into the condensation cell, the vapor components except helium were nearly completely trapped in the condensation cell. The pressure drop from the equilibrium cell to the atmosphere was so small that the pressures in the equilibrium cell and the condensation cell were considered to be of ambient pressure. When the amount of vapor-phase sample condensed reached 1−2 g, the carrier gas flow was stopped. The decrease of the feed sample was determined by weighing the equilibrium cell, and the total amount of helium gas supplied was recorded. The compositions of the liquid mixture trapped in the condensation cell were determined by gas chromatography.

The total pressures and vapor−liquid equilibrium compositions for monocarboxylic acid + monocarboxylic acid binary systems were determined as follows. The following assumptions are valid because the total pressure in this experiment is atmospheric pressure:

(a) The solubility of helium in this liquid mixture is negligible.

(b) The monomer and dimer of carboxylic acid, cross(hetero)-dimer, and helium exist in the vapor phase, and they compose an ideal gaseous mixture.

(c) Association constants of carboxylic acids are not affected by the presence of helium.

Because helium gas can be treated as inert, this experiment is similar to a simple distillation. Therefore, the following Rayleigh's equation can be adopted:

$$\ln\left(\frac{L^{\mathrm{f}}}{L^{\mathrm{s}}}\right) = \int_{x_1^{\mathrm{s}}}^{x_1^{\mathrm{f}}} \frac{\mathrm{d}x_1}{y_1 - x_1} \qquad (1)$$

where L is the amount of the sample in the equilibrium cell and x_1 and y_1 are the compositions of component 1 in the liquid and vapor phases, respectively. Superscripts s and f denote the start and final states of the experiment, respectively. Liquid-phase composition x_1, vapor-phase composition y_1, and the total pressure p change continuously during an experiment. To apply eq 1 to the present experiment, an average vapor-phase composition y_1^{av} was first determined. Then, the average liquid-phase composition x_1^{av} and the average total pressure p^{av}, which give the vapor−liquid equilibrium relation, were determined.

The vapor carried with the helium gas from the equilibrium cell was almost all trapped in the condensation cell because the temperature in the condensation cell is low enough. The average vapor-phase composition y_1^{av} was approximated by the composition of the liquid mixture in the condensation cell. The composition was determined by the peak areas and the relative sensitivity (factor) of the gas chromatograph. The factors were determined by using standard solutions with known compositions.

Next, the average liquid-phase composition x_1^{av} was determined as follows. The relative volatility β_{12} is defined by the following equation:

$$\beta_{12} \equiv (y_1/x_1)/(y_2/x_2) = (y_1/x_1)/\{(1 - y_1)/(1 - x_1)\} \qquad (2)$$

Assuming that the relative volatility β_{12} is constant as the average value β_{12}^{av} in a short range of the composition between x_1^{s} and x_1^{f} (usually Δx_1 was within 0.05 near $x_1^{\mathrm{s}} = 0.5$, for example), the following equations can be derived from eqs 1 and 2:

$$\ln\frac{L^{\mathrm{s}}}{L^{\mathrm{f}}} = \frac{1}{\beta_{12}^{\mathrm{av}} - 1}\ln\left\{\frac{x_1^{\mathrm{s}}(1 - x_1^{\mathrm{f}})}{x_1^{\mathrm{f}}(1 - x_1^{\mathrm{s}})}\right\} + \ln\frac{(1 - x_1^{\mathrm{f}})}{(1 - x_1^{\mathrm{s}})} \qquad (3)$$

$$\beta_{12}^{\mathrm{av}} = (y_1^{\mathrm{av}}/x_1^{\mathrm{av}})/\{(1 - y_1^{\mathrm{av}})/(1 - x_1^{\mathrm{av}})\} \qquad (4)$$

Further, L^{f} and x_1^{f} were obtained from the material balance of the liquid mixture in the equilibrium cell by using the equations

$$L^{\mathrm{f}} = L^{\mathrm{s}} - (n_1 + n_2) \qquad (5)$$

$$x_1^{\mathrm{f}} = \frac{L^{\mathrm{s}}}{L^{\mathrm{f}}}x_1^{\mathrm{s}} - \left(\frac{L^{\mathrm{s}}}{L^{\mathrm{f}}} - 1\right)y_1^{\mathrm{av}} \qquad (6)$$

where n_i is the amount of component i carried away from the equilibrium cell, which can be determined from the decrease of the amount in the equilibrium cell. It can be obtained by solving the following simultaneous equations:

$$W^{\mathrm{s}} - W^{\mathrm{f}} = n_1M_1 + n_2M_2 \qquad (7)$$

$$y_1^{\mathrm{av}} = \frac{n_1}{n_1 + n_2} \qquad (8)$$

where W is the weight of the liquid mixture in the equilibrium cell, M is the molar mass, and subscripts 1 and 2 indicate components 1 and 2, respectively. Based on W^{s}, W^{f}, x_1^{s}, and y_1^{av} measured, the relative volatility β_{12}^{av} can be calculated with eq 3. Therefore, the average liquid-phase composition x_1^{av} corresponding to y_1^{av} was determined with eq 4.

Then, the average total pressure p^{av} was determined as follows. On the basis of the pVT relation of an ideal gaseous mixture for the monomer and dimer of carboxylic acids and helium in the equilibrium cell, the partial pressures were calculated as follows:

$$p_{1\mathrm{m}}^{\mathrm{av}}V = n_{1\mathrm{m}}RT \tag{9}$$

$$p_{1\mathrm{d}}^{\mathrm{av}}V = n_{1\mathrm{d}}RT \tag{10}$$

$$p_{2\mathrm{m}}^{\mathrm{av}}V = n_{2\mathrm{m}}RT \tag{11}$$

$$p_{2\mathrm{d}}^{\mathrm{av}}V = n_{2\mathrm{d}}RT \tag{12}$$

$$p_{12\mathrm{d}}^{\mathrm{av}}V = n_{12\mathrm{d}}RT \tag{13}$$

$$p_{\mathrm{He}}^{\mathrm{av}}V = n_{\mathrm{He}}RT \tag{14}$$

where

$$n_1 = n_{1\mathrm{m}} + 2n_{1\mathrm{d}} + n_{12\mathrm{d}} \tag{15}$$

$$n_2 = n_{2\mathrm{m}} + 2n_{2\mathrm{d}} + n_{12\mathrm{d}} \tag{16}$$

and

$$\pi = p_{1\mathrm{m}}^{\mathrm{av}} + p_{1\mathrm{d}}^{\mathrm{av}} + p_{2\mathrm{m}}^{\mathrm{av}} + p_{2\mathrm{d}}^{\mathrm{av}} + p_{12\mathrm{d}}^{\mathrm{av}} + p_{\mathrm{He}}^{\mathrm{av}} \tag{17}$$

where p_i^{av} is the partial pressure of each component i and V is the volume which all components occupy at temperature T and atmospheric pressure π. Subscripts m and d indicate the monomer and the dimer of carboxylic acids, respectively. Subscript He denotes helium.

The partial pressures of the monomer and the dimer of carboxylic acids are related by an association constant. In general, the association constant of each dimer is given as a function of the temperature[5] by

$$K_i = \frac{p_{i\mathrm{d}}}{p_{i\mathrm{m}}^{\ 2}}f^{\circ} = \exp\left(\frac{\Delta S_i}{R} - \frac{\Delta H_i}{RT}\right) \tag{18}$$

where $f^{\circ} = 101.3$kPa and ΔS_i and ΔH_i are the entropy and enthalpy for association, respectively. We used -149.0 J·mol^{-1}·K^{-1} for ΔS_i and -58.5 kJ·mol^{-1} for ΔH_i for formic acid and -136.0 J·mol^{-1}·K^{-1} for ΔS_i and -58.5 kJ·mol^{-1} for ΔH_i for other acids.[6] The association constant for a cross(hetero)-dimer[7] is

$$K_{ij} = \frac{p_{ij\mathrm{d}}}{p_{i\mathrm{m}}p_{j\mathrm{m}}}f^{\circ} = 2\sqrt{K_iK_j} \tag{19}$$

On the basis of eqs 9−19, the average partial pressure p_i^{av} can be obtained and the average total pressure p^{av} can be calculated with

$$p^{\mathrm{av}} = p_{1\mathrm{m}}^{\mathrm{av}} + p_{1\mathrm{d}}^{\mathrm{av}} + p_{2\mathrm{m}}^{\mathrm{av}} + p_{2\mathrm{d}}^{\mathrm{av}} + p_{12\mathrm{d}}^{\mathrm{av}} \tag{20}$$

The present experimental procedure can be applied to obtain the vapor-phase and liquid-phase compositions (x_1^{av} and y_1^{av}) of any other systems containing nonassociating components. The average total pressure of such systems can also be determined by neglecting the unnecessary dimer terms in eqs 9−20.

Table 2. Vapor−Liquid Equilibria for the Ethanol (1) + Toluene (2) System at 323.2 K

x_1	y_1	p/kPa
0.009	0.171	14.14
0.444	0.672	31.72
0.485	0.680	31.66
0.981	0.961	29.96

Table 3. Vapor−Liquid Equilibria for Carboxylic Acid + Carboxylic Acid Systems

formic acid (1) + acetic acid (2) at 343.2 K			acetic acid (1) + butyric acid (2) at 358.2 K		
x_1	y_1	p/kPa	x_1	y_1	p/kPa
0.020	0.034	19.6	0.018	0.072	5.0
0.048	0.078	20.2	0.044	0.164	5.5
0.098	0.152	21.4	0.090	0.291	6.6
0.294	0.393	25.6	0.281	0.606	11.2
0.494	0.588	29.0	0.484	0.776	17.0
0.696	0.762	32.8	0.690	0.884	23.3
0.899	0.921	36.1	0.897	0.963	30.4
0.949	0.960	36.8	0.948	0.982	33.2
0.980	0.984	37.2	0.980	0.993	34.1

formic acid (1) + propionic acid (2) at 343.2 K			propionic acid (1) + butyric acid (2) at 358.2 K		
x_1	y_1	p/kPa	x_1	y_1	p/kPa
0.017	0.081	7.2	0.019	0.039	4.8
0.040	0.164	8.2	0.048	0.093	5.0
0.088	0.292	10.1	0.095	0.176	5.3
0.275	0.572	16.7	0.296	0.458	6.6
0.485	0.733	23.6	0.494	0.661	8.2
0.691	0.840	29.8	0.691	0.817	9.8
0.898	0.940	35.2	0.896	0.944	11.8
0.949	0.968	36.5	0.948	0.973	12.2
0.980	0.988	37.3	0.980	0.990	12.6

acetic acid (1) + propionic acid (2) at 343.2 K		
x_1	y_1	p/kPa
0.019	0.039	6.7
0.048	0.093	7.1
0.096	0.179	7.6
0.289	0.447	9.9
0.486	0.647	12.0
0.692	0.807	14.6
0.897	0.940	17.4
0.948	0.970	18.0
0.980	0.988	18.4

Results and Discussion

Experimental Data. The experimental results of x_1^{av}, y_1^{av}, and p^{av} are presented as x_1, y_1, and p in Tables 2 and 3. To confirm the reliability of this experiment, the results for ethanol + toluene obtained at 323.2 K were compared with the literature values. The p−x−y relation is shown in Figure 2 together with that reported by Zharov et al.[8] and by Miyamoto et al.[2] Both data in the literature were evaluated and found to be thermodynamically consistent.[1,2] Good agreement between the present data and the literature values is shown, which confirms the reliability of the apparatus and procedure.

Among the vapor−liquid equilibria for monocarboxylic acid binary systems listed in Table 3, a typical illustration is shown in Figure 3 for formic acid + acetic acid. It is estimated that the uncertainties of this experiment are ±0.1 K for temperature, ±0.5 kPa for pressure, and ±0.003 mole fraction for composition. The thermodynamic consistency tests[1] (area test and point test) were performed and shown in Table 4 for the present binary systems as well as the monocarboxylic acid binary systems reported in the literature.[1] As shown in Table 4, the area test for the present systems seems to be better than that for the literature values. However, the area test is slightly greater than the consistency level because the homologous monocarboxylic acid binary systems are close to an ideal solution. On the other hand, all of the present systems are eligible for the point test, though some of the literature values are inconsistent. Judging from this consideration, the present data are believed to be reliable.

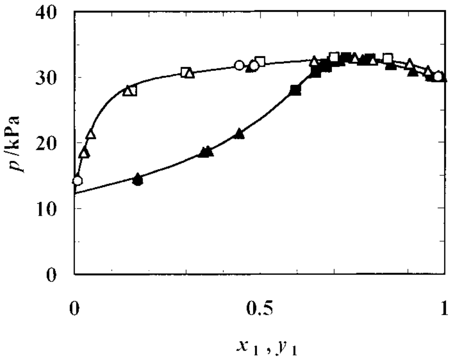

Figure 2. Vapor–liquid equilibria for the ethanol (1) + toluene (2) system at 323.2 K: (□, ■) Zharov et al.;[8] (△, ▲) Miyamoto et al.;[2] (○, ●) present work; (—) correlation with the NRTL model.

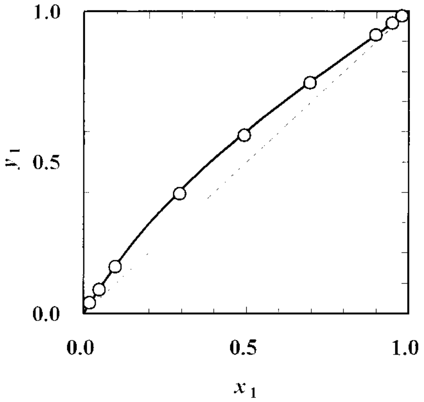

Figure 3. Vapor–liquid equilibria for the formic acid (1) + acetic acid (2) system at 343.2 K: (○) present work; (—) correlation with the NRTL + vapor-phase association model.

Correlation. The fugacities of each component in the vapor phase and the liquid phase are equal under vapor–liquid equilibrium conditions. According to the theory of associated solutions, the fugacity of the monomer is equal to that of the component.[9] Therefore, vapor–liquid equilibrium for an associating component binary system is expressed by the equations.[10]

$$f_i^{L} = f_i^{V} = f_{im}^{V} \tag{21}$$

With the mole fractions denoted by η, the fugacities of each component in the vapor and liquid phases are given as

$$f_{im}^{V} = p\eta_{im}\varphi_{im} \tag{22}$$

$$f_i^{L} = \gamma_i x_i f_i^{0L} \tag{23}$$

If we can assume that the monomer and dimer of carboxylic acid exist in the vapor phase and they are an ideal gaseous mixture, the fugacity coefficients can be obtained by the following equation because the total pressure is sufficiently low.

$$\varphi_{im} = 1 \tag{24}$$

The relationships among the mole fraction η, the association constant K, and the mole fraction of acid y are given by

$$\eta_{1m} + \eta_{1d} + \eta_{2m} + \eta_{2d} + \eta_{12d} = 1 \tag{25}$$

$$K_i = \frac{p_{id}}{p_{im}^{2}} f^{\circ} = \frac{\eta_{id}}{p\eta_{im}^{2}} f^{\circ} \tag{26}$$

$$K_{ij} = \frac{p_{ijd}}{p_{im}p_{jm}} f^{\circ} = \frac{\eta_{ijd}}{p\eta_{im}\eta_{jm}} f^{\circ} \tag{27}$$

$$y_1 = \frac{\eta_{1m} + 2\eta_{1d} + \eta_{12d}}{\eta_{1m} + 2\eta_{1d} + \eta_{2m} + 2\eta_{2d} + 2\eta_{12d}} \tag{28}$$

The liquid-phase fugacity for a pure component can be obtained by the following equations by adopting the mole fraction of the monomer η_{im}^{0} in the saturated vapor phase at the same temperature of the binary system ($\varphi_{im}^{0} = 1$).

$$f_i^{0L} = f_{im}^{0V} = p_i^{sat}\eta_{im}^{0}\varphi_{im}^{0} = p_i^{sat}\eta_{im}^{0} \tag{29}$$

$$\eta_{im}^{0} + \eta_{id}^{0} = 1 \tag{30}$$

$$K_i = \frac{p_{id}}{p_{im}^{2}} f^{\circ} = \frac{\eta_{id}^{0}}{p_i^{sat}(\eta_{im}^{0})^{2}} f^{\circ} \tag{31}$$

The saturated vapor pressures can be calculated with the Antoine equation with parameters in Table 1. Finally, the fundamental equation of vapor–liquid equilibria (eq 21)

Table 4. Thermodynamic Consistency[a]

component 1	component 2	area test	point test	γ	condition	lit.
formic acid	acetic acid	38	0.003	$1.01 < \gamma < 1.18$	343.2 K	this work
formic acid	propionic acid	13	0.004	$1.01 < \gamma < 1.74$	343.2 K	this work
acetic acid	propionic acid	52	0.001	$1.01 < \gamma < 1.15$	343.2 K	this work
acetic acid	butyric acid	29	0.002	$1.00 < \gamma < 1.23$	358.2 K	this work
propionic acid	butyric acid	+[b]	0.001	$0.99 < \gamma < 1.06$	358.2 K	this work
formic acid	acetic acid	93	0.010	$0.78 < \gamma < 1.43$	101.3 kPa	1
formic acid	acetic acid	+[b]	0.008	$1.01 < \gamma < 1.10$	101.3 kPa	1
formic acid	acetic acid	48	0.008	$0.99 < \gamma < 1.11$	101.3 kPa	1
formic acid	acetic acid	107	0.016	$1.00 < \gamma < 1.16$	26.7 kPa	1
acetic acid	propionic acid	27	0.018	$0.79 < \gamma < 1.09$	101.3 kPa	1
acetic acid	propionic acid	9.2	0.022	$0.77 < \gamma < 1.08$	101.3 kPa	1
thermodynamic consistency[a]		≤10	≤0.01			

[a] Gmehling and Onken.[1] [b] Consistency for neary ideal systems with $0.95 < \gamma < 1.10$.[1]

Table 5. Parameters for the NRTL Model and Average Deviations

component 1	component 2	$[(g_{12} - g_{22})/R]$/K	$[(g_{21} - g_{11})/R]$/K	α_{12}	Δy	Δp/kPa
formic acid	acetic acid	61.543	−5.182	0.707	0.004	0.46
formic acid	propionic acid	170.727	22.738	0.642	0.004	0.36
acetic acid	propionic acid	161.157	−83.963	0.716	0.001	0.21
acetic acid	butyric acid	186.488	−69.408	0.623	0.002	0.54
propionic acid	butyric acid	177.501	−120.635	0.614	0.002	0.10

can be rewritten as

$$p\eta_{im} = \gamma_i x_i p_i^{sat} \eta_{im}^0 \tag{32}$$

Activity coefficients γ_1 and γ_2 were evaluated by eqs 25−28 and 30−32 with the present experimental data. The ranges of activity coefficients are presented in Table 4. Activity coefficients obtained were correlated by the NRTL model.[11] Parameters for the NRTL model were optimized by the objective function

$$\mathrm{OF} = \sum_{k=1}^{N}[(\gamma_{1,\mathrm{exptl}} - \gamma_{1,\mathrm{calcd}})^2 + (\gamma_{2,\mathrm{exptl}} - \gamma_{2,\mathrm{calcd}})^2]_k \tag{33}$$

The optimized parameters are listed in Table 5. The vapor-phase compositions and the total pressures calculated by the NRTL model at given liquid-phase compositions were compared with the experimental data. The correlation performance Δy and Δp for all binary systems are listed in Table 5, and a typical illustration for formic acid + acetic acid is shown in Figure 3 with good agreement.

Nomenclature

f = fugacity (kPa)
g = NRTL parameter (J·mol^{-1})
ΔH = enthalpy change (J·mol^{-1})
K = association constant
L = amount of liquid in the equilibrium cell (mol)
M = molar mass (g·mol^{-1})
N = number of data points
n = amount of substance (mol)
OF = objective function
p = pressure (kPa)
R = gas constant (J·mol^{-1}·K^{-1})
ΔS = entropy change (J·mol^{-1}·K^{-1})
T = temperature (K)
V = volume (mL)
W = weight of liquid in the equilibrium cell (g)
x = mole fraction of component in the liquid phase
y = mole fraction of component in the vapor phase

Greek Letters

α = NRTL parameter
β = relative volatility
γ = activity coefficient
η = mole fraction
π = atmospheric pressure (kPa)
φ = fugacity coefficient

Subscripts

1, 2 = components 1 and 2
calcd = calculated value
d = dimer
exptl = experimental value
He = helium
i, j = components i and j
k = data point
m = monomer

Superscripts

av = average value
f = final state
L = liquid phase
s = starting state
sat = saturated state
V = vapor phase
0 = pure substance
° = standard state

Literature Cited

(1) Gmehling, J.; Onken, U. A., Eds. *Vapor−Liquid Equilibrium Data Collection*; *Chemistry Data Series*; DECHEMA: Frankfurt/Main, Germany, 1977.
(2) Miyamoto, S.; Nakamura, S.; Iwai, Y.; Arai, Y. Measurement of Isothermal Vapor−Liquid Equilibria for Hydrocarbon + Monocarboxylic Acids Binary Systems by a Flow-Type Apparatus. *J. Chem. Eng. Data* **2000**, *45*, 857−861.
(3) Yaws, C. L. *Thermodynamic and Physical Property Data*; Gulf Publishing Co.: Houston, 1992.
(4) Ambrose, D.; Ghiassee, N. B. Vapor Pressures and Critical Temperatures and Critical Pressures of Some Alkanoic Acids: C_1 to C_{10}. *J. Chem. Thermodyn.* **1987**, *19*, 505−519.
(5) Jasperson, L. V.; Wilson, L. C.; Brady, C. J.; Wilding, W. V.; Wilson, G. M. Vapor Association of Monocarboxylic Acids from Heat of Vaporization and PVT Measurements. *AIChE Symp. Ser.* (*DIPPR*) **1989**, *85*, 102−139.
(6) Miyamoto, S.; Nakamura, S.; Iwai, Y.; Arai, Y. Measurement of Vapor-Phase Compressibility Factors of Monocarboxylic Acids Using a Flow-Type Apparatus and Their Association Constants. *J. Chem. Eng. Data* **1999**, *44*, 48−51.
(7) Prausnitz, J. M.; Lichtenthaler, R. N.; Azevedo, E. G. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1986.
(8) Zharov, V. T.; Morachevsky, A. G.; Shapil, L. G.; Buevich, T. A. One of the Forms of the Dependence of the Partition Function on the Composition of the Solution and the Use of the Equations for Calculating Data of Liquid−Vapor Equilibria in Ternary Systems. *Zh. Prikl. Khim.* **1968**, *41*, 2443−2450.
(9) Saito, S. *Fundamentals for Prediction of Equilibrium Properties Based on Statistical Thermodynamics (in Japanese)*; Baifukan: Tokyo, 1983.
(10) Tochigi, K.; Kojima, K. Activity Coefficients at Infinite Dilution for Binary Systems Containing an Association Substance. *J. Chem. Eng. Jpn.* **1977**, *10*, 343−348.
(11) Renon, H.; Prausnitz, J. M. Local Composition in Thermodynamic Excess Function for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135−144.

Received for review July 12, 2000. Accepted December 6, 2000.

JE000205N